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Transactions of the Faraday Society

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TO PROMOTE THE STUDY OF ELECTROCHEMISTRY ELECTROMETALLURGY CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS

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VOL. IX. JULY, 1913. PARTS 1 AND 2.

GENERAL DISCUSSION ON "MAGNETIC PROPERTIES OF ALLOYS."

(*Further Communication to Discussion, received January* 10, 1913.)

Mr. James Aston (Cincinnati): The paper of Professor Gumlich on the "Magnetic Properties of the Iron-Silicon Alloys" is extremely interesting and important, not only for the data introduced regarding the specific influence of silicon on the magnetic quality of iron, but especially in view of the deductions as to the effect of silicon on the state of the carbon. The observations on the precipitation of temper carbon in steels of very low carbon content have an important bearing on the interpretation of the iron-carbon diagram, and it would appear to be evidence in support of the iron-cementite system as the primary or stable one; and also evidence that graphite appears largely as a result of secondary influences, of which silicon, coupled with the effect of heat, is the principal one.

As regards the magnetic quality, the hypothesis advanced in the early days of the new electrical steels was that the silicon acting as a deoxidizing agent purified the iron, and its effect on the deleterious foreign inclusions was more than enough to offset that of the excess silicon remaining as such, or of any inclusion which might remain in an altered condition. Professor Gumlich's conclusion is that the effect of the silicon on the permeability is twofold; to keep such carbon as may be present, in the form of free cementite, rather than in the more harmful solution or austenitic state; and furthermore, that with enough silicon present, and sufficient temperature and time of annealing, the cementite is decomposed into iron and temper carbon. Thus the predominant effect is one of nearer approach to the magnetic quality of pure ferrite, and a choosing of the lesser of two evils.

While it appears likely that some beneficial effect of the silicon is manifested in accordance with both of the hypotheses advanced above, it would seem as though its greatest influence is a structural one; or as expressed by Arnold and Hicks,* "The elements giving iron high permeability and low coercive force are those which cause it to crystallize in large crystals." It seems true, other things being equal, that the heat treatment which will give to pure iron a coarseness of crystallization, and above all a uniformity and regularity of such structure, will be accompanied by a low coercive force,

* *Nature*, April 17, 1902.

and the effect of heat treatment is augmented by the addition of silicon, or analogous elements, as arsenic or tin, all of which increase the coarseness of crystallization of the material.

The work of Terry* upon the effect of annealing on the magnetic properties of electrolytic iron shows a falling off in coercive force from 3·80 to as low as 0·53, and a reduction of hysteresis loss to less than one-fifth of the original by heating to temperatures up to 1,100 to 1,200° C. This result was upon material of very high purity (99·97 per cent. iron) with a carbon content of 0·01 or less; the effect of the heat, therefore, was solely upon the grain structure. Furthermore, investigations on the magnetic properties of electrolytic iron and other high purity products, where the carbon content is 0·02 or less, or so small as to be negligible, have shown the beneficial result of silicon additions. Also, in the case of sheet steels of ordinary composition (not silicon steel) the magnetic quality seems to be more dependent upon the heat treatment as affecting the grain structure than upon the actual differences in the small amounts of carbon present. Professor Gumlich's photomicrographs are in line with this argument, in showing a larger grain size or coarseness of crystallization of the pearlite areas than is usually associated with the carbon content of the material such as he used.

The influence of symmetry of the crystal aggregate upon the hysteresis loss is very striking in the case of high purity, high silicon material, upon testing it as it comes from the hot rolls, or after giving it a single cold rolling pass, or after the usual annealing treatment. The hysteresis losses may be taken as 75, 110, and 45 respectively; and the distortion or regularity of grain as a result of the different treatments is very evident under the microscope. Here we have an extreme influence of a structural nature solely, since the carbon content is negligible.

It would seem as though the silicon serves a triple purpose: (1) as a cleansing or deoxidizing agent; (2) through its effect on the state of the carbon; (3) but especially in acting with heat treatment to promote symmetry of crystallization, or analogous beneficial structural effect.

* *Phys. Rev.*, February, 1910.

THE BILLITER ALKALI-CHLORINE CELLS.

By A. J. ALLMAND, D.Sc.

(*A Paper read before the Faraday Society, Tuesday, November 26, 1912, Dr. H. Borns in the Chair.*)

The most important advances made in late years in the technical electrolysis of alkaline chlorides for the production of caustic alkali and chlorine are perhaps due to Dr. Jean Billiter, Privatdozent in the University of Vienna. Some years back he designed a diaphragm cell which is being exploited by Siemens and Halske, and recently he has invented a modified form of the well-known bell-jar cell, which is undoubtedly, taken all in all, one of the most efficient cells now operated technically. The Billiter-Siemens diaphragm cell I propose to mention briefly only, as full accounts of it are available elsewhere,* and shall devote most attention to the Billiter "membrane" cell, the first installation of which started work early this year.

Billiter-Siemens Cell.

Most diaphragm cells in technical use have vertical diaphragms (*e.g.*, Hargreaves-Bird, Townsend, Finlay). Billiter, however, has returned to the use of horizontal diaphragms such as were formerly employed by Le Sueur and by Carmichael. He has compared elsewhere the relative advantages and disadvantages of the vertical and horizontal arrangements. A horizontal diaphragm is more slowly attacked chemically, as it remains more or less saturated with the alkali which migrates upwards from the cathode situated immediately underneath. This is particularly important when making strong alkaline liquors. Further, the hydrostatic pressure on it is uniform at all points, not varying with the height as in vertical diaphragms. This means a more uniform flow of liquid through, and consequently a more efficient checking of the movement of the OH' ions towards the anode. There are corresponding structural disadvantages. The floor-space needed is greater. Further, the insides of the cells are less easily accessible and the anodes are necessarily of more complicated construction.

The active diaphragm material in the Billiter-Siemens cell consists of a mixture of asbestos wool and $BaSO_4$, spread out evenly on top of a sheet of woven asbestos cloth, which in its turn rests on the iron-wire network which constitutes the cathode. The function of the asbestos cloth is merely to support the $BaSO_4$ mixture and to prevent its being displaced by the lively hydrogen evolution. The cathode makes contact with the iron bottom of a trough, the sides of which are lined with cement, and the anode chamber is formed by a non-conducting bell-jar which is securely cemented around the edges of the diaphragm. An important feature of the cell is the arrangement

* Billiter, *Die elektrochemischen Verfahren der chemischen Gross-Industrie*, ii., 215 ff. *Die elektrolytische Alkalichloridzerlegung mit starren Metallkathoden*, i., 119, 191. See also Allmand, *Principles of Applied Electrochemistry*, p. 375. Also *Chemiker Zeitung*, 1911, p. 573; *Der Papier Fabrikant*, 1911, Parts 1, 11, 33; *Wochenblatt für Papierfabrikation*, 1011, Parts 19, 42.

for heating the electrolyte by means of earthenware pipes through which hot liquids run, these being immersed in the brine at the top of the bell-jars.

Cells have been made carrying up to 3,000 amperes at a current density of 4–6 $\frac{\text{amps.}}{\text{d.m.}^2}$. Working at 85–90°, 12–16 per cent. NaOH or 18–20 per cent. KOH can be made at a 95 per cent. cathodic current efficiency, employing 3·5 volts.

An interesting laboratory study of the Billiter-Siemens cell has been recently published by Mühlhaus.* He finds that the $BaSO_4$ used for the diaphragm is best precipitated hot. No change of size of grain when in the hot liquors of the Billiter cell is then likely to take place, and a regular and uniform liquid flow is thus assured. The highest current density permissible is 6–7 $\frac{\text{amps.}}{\text{d.m.}^2}$. Above this limit, disintegration sets in. Using 30–32 per cent. brine at ordinary temperatures, the following figures were obtained :—

Concentration of Alkali.	Current Efficiency. Per Cent.
3n.	98–99
4n.	95–97
5n.	80–85
6n.	75

The chlorine gas fell in purity from 99·5 per cent. to 92 per cent. as the alkali concentration was increased. The oxygen produced exceeded the amount of CO_2. The solid caustic resulting contained considerable quantities of $NaClO_3$ if produced from liquors stronger than 4n. † The best results on the whole were given when making 4n. NaOH at a current density of 4 $\frac{\text{amps.}}{\text{d.m.}^2}$. Raising the working temperature to 70–80° improved both energy efficiency and purity of alkali.

The Billiter-Siemens process is now operated as follows :—

(*a*) In Aschersleben, Saxony, by the Kaliwerke Aschersleben A.G. Ten 2,000-ampere units.

(*b*) In Höchst, by the Farbwerke Höchst.

(*c*) In Brückl, Bosnia, by the Bosnische Elektrizitäts A.G. Sixty-four 2,500-ampere units.

(*d*) In Krumau, Bohemia, by Ignaz Spiro und Söhne. Thirty-two 500-ampere units.

(*e*) At Niagara Falls, by the Niagara Alkali Company. A 1,000-k.w. installation of 3,000-ampere units.

A number of plants are also being installed or enlarged. The Niagara Alkali Company (which has succeeded the old Roberts Chemical Company), is at present increasing the size of its plant from 1,000 to 3,000 kilowatts. It has also been made known that a new factory for caustic alkali and bleach is being erected, commencing with 78 2,000-ampere units, and that a textile factory is installing 24 100-ampere units.

Billiter-Leykam Cell.

In this cell ‡ Billiter has successfully modified the bell-jars process, placing the cathodes (hooded to collect the hydrogen) immediately *underneath* the bell-jar, and not around its sides, as in the Aussig cell. (Similar constructions

* Dissertation (Dresden, 1911).

† But only at room temperature. Experiments carried out at higher temperatures, corresponding to technical conditions, showed no such presence of chlorate.

‡ British Patent, 11,693 (1910) ; *Principles of Applied Electrochemistry*, p. 373.

had been formerly suggested by Richardson * and by Bein,† but had achieved no technical success.) By doing this, Billiter gains an important advantage. In the ordinary bell-jar cell, both flow of liquid and flow of current change in direction at the lower edge of the bell-jar. This results in non-uniformity of current density and liquid flow in the different parts of the bell-jar section. At some points liquid will be flowing more quickly than is necessary to overcome the OH' migration towards the anode, at other points the contrary will be true: the movement of the OH' ions will predominate, and the current efficiency will fall. This last statement particularly holds for those parts of the bell-jar section farthest removed from the walls, where the current of

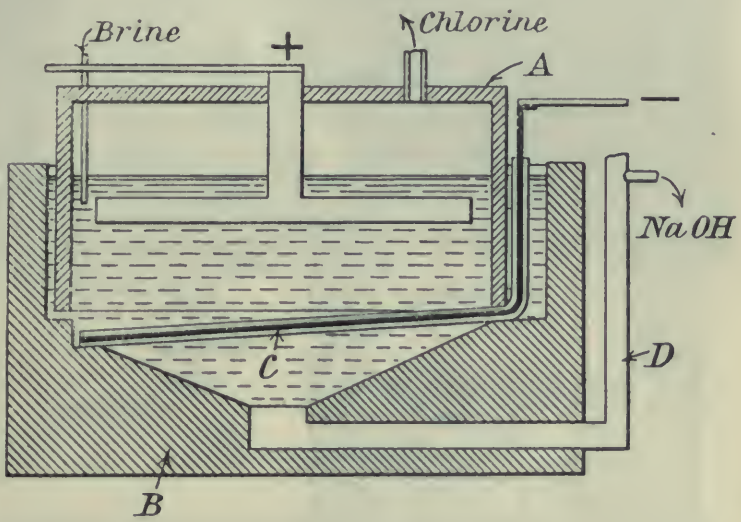

FIG. 1.

liquid is exceedingly slow. The larger the bell-jar, the greater proportionately is this disturbance. It also increases rapidly with current density. The consequence is that the units (bell-jars) at Aussig are very small, and can only be worked at a low current density, furnishing weak alkali. Such a plant requires much floor space for its output and the labour charges are high.

In the Billiter cell, this change of direction and the resulting irregularities are avoided, the motion of the brine being directly opposed to that of the current lines until it has passed the cathodes. The consequence is that high current densities can be used, stronger caustic liquors produced, high current efficiencies obtained, and large units constructed. At the same time, the advantage of the bell-jar cell—the absence of diaphragms—is essentially retained. For, though the *current* must all pass through the hoods which cover the cathodes, this is not true of the electrolyte. Most of it passes directly through the spaces between neighbouring cathodes, and is charged with caustic by diffusion from the concentrated alkali which fills the cathode hoods. Not only does this alkali protect the hood material (in practice, woven asbestos) against chemical action of chlorine compounds, but suspended matter present in the brine is not filtered out, as happens in

* British Patent, 5,694 (1893). † British Patent, 24,058 (1899).

diaphragm cells, and *it is not necessary to purify the brine in any way*. The asbestos hoods are made of as coarse a structure as is consistent with their function of leading off the hydrogen gas, and affect the voltage to a very slight degree only. Finally, the cell is heated in a similar fashion to the Billiter-Siemens cell, and the voltage thus lowered.

The essential parts of the Billiter-Leykam cell are shown diagrammatically in Figs. 1 and 2. *A* is the bell-jar inverted in the cement trough *B*, and provided with anode outlet for chlorine, inlet for brine and heating arrangement (not shown). The cathodes *C* are arranged below the bottom level of *A* and consist in practice of T-iron. They are enclosed separately in long woven asbestos tubes, which are suitably braced in order to avoid deformation by the

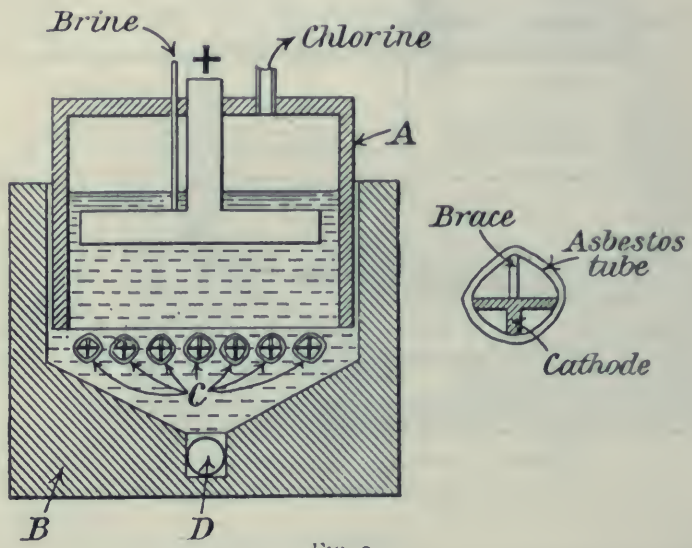

FIG. 2.

evolved hydrogen, and are slanted sufficiently to allow the gas to stream away readily. These cathodes project out into a side compartment of the cell as shown, from which the hydrogen can, if necessary, be collected. The causticized brine flows off through *D*.

The Austrian rights to the Billiter bell-jar cell have been purchased by the paper manufacturers, Leykam-Josefsthal A.G. The first plant has been erected in their factory at Gratwein, a village on the Austrian Southern Railway, a few miles from Graz, has been in continued operation since early this year, and has given every satisfaction. Some 1,700–1,800 kilos of active chlorine are produced daily, and the whole plant uses about 400 P.S.*—350 P.S. for the cells and 50 P.S. for auxiliary pumps, fan, etc. Power is purchased from a company at 150 kr. (£6 5s.) per P.S. year. After converting into direct current, and reckoning all losses in leads, &c., the cost comes to 180 kr. (£7 10s.) per P.S. year.

The plant consists of 56 1,200-ampere units, 50 of which were working at the time of my visit last July. The cells (Fig. 3) are 5·5 metres long, 1·1 metres broad

* The P.S. and P.S. year are of course about 1⅓ per cent. smaller than the corresponding H.P. and H.P. year units.

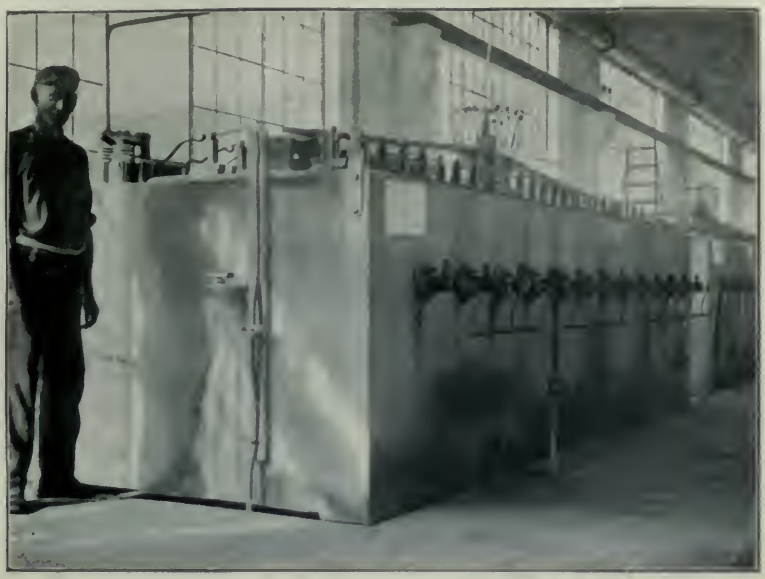

Fig. 3.

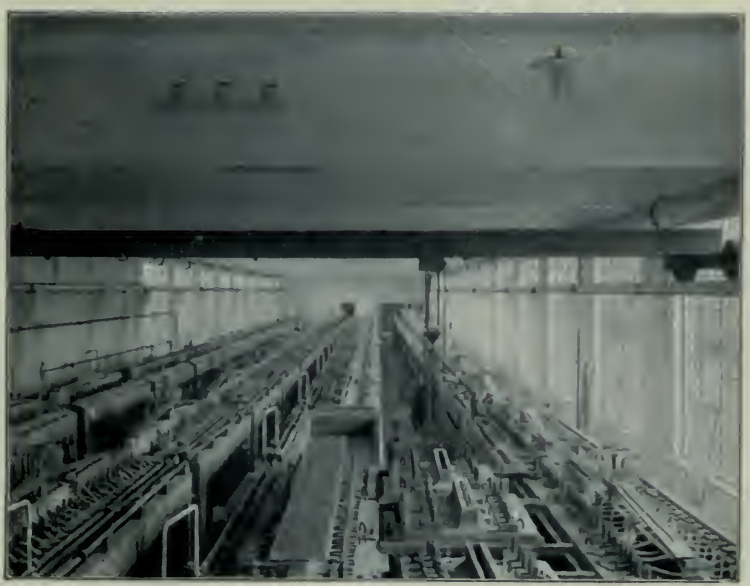

Fig. 4.

(internal measurements) and about 1·3 metres high. The side walls commence to slope inwards about 70 cm. below the top of the cell. They are built of reinforced concrete, the upper part being lined with earthenware bricks set in cement. They are provided with three cement lids, each of which carries eight anodes. The latter are of Acheson graphite (1·0 × 0·18 × 0·05 metre), each being led through its lid by means of two graphite rods. The lids are cemented on to a shallow shelf cut out of the wall of the cell by means of ordinary putty, which stands the action of chlorine very well and always remains fairly soft. Putty is also used at the points where the anodes pass through the lids. Each anode takes 50 amperes at a current density, assuming lower and side surfaces to be active, of about 1·6–1·7 $\frac{\text{amps.}}{\text{d.m.}^2}$.

The cathodes are of T-iron and enclosed in woven asbestos tubes. These taper down slightly towards their closed lower ends, and the whole is braced by the insertion of a wedge-shaped strip of asbestos cement. The tubes pass through holes in the dividing wall into the side compartment of the cell as indicated in Fig. 1. Two iron rods attached to each T-iron cathode take the current to the copper leads above. The hydrogen is allowed to escape. The cathodes are, of course, about 1 metre in length, and the mean breadth of the asbestos tubes is about 5 cm. Between each tube there is a space of 5 to 8 mm. The upward slope of these tubes is about 2 cm. per metre.

The brine (moving from a reservoir under gravity) is led to a distributing box situated above the cell. From this it proceeds by way of a series of short capillary tubes (1·5 mm. bore) to 22 tin tubes, which pass through the cell lids, and is thus fed in between the anodes. Regulation of the main supply to the cell is effected by means of a rubber tube and clip. This arrangement acts on the whole very satisfactorily, though the capillaries sometimes get stopped up. The causticized brine is drawn off from one side of the cell by means of siphon overflows. Three are provided, but one only is used in practice.

The heating arrangement used by Dr. Billiter in his diaphragm cell, though available for all other installations of his "membrane" cell, cannot* be used at Gratwein. The cells are therefore provided with a heating arrangement which employs steam, the details of which, however, I cannot divulge here. When I was in Gratwein the cells were being mostly worked at room temperature, whilst those few which were being heated were working at 65° to 70°. The cost of the steam used is very small.

The cells are arranged in four rows, two rows being worked in series, and are insulated by glass resting on concrete supports. Beneath the cells are arranged the chlorine and brine pipes, and a channel for the caustic liquors. The chlorine pipe-line is constructed of cement, junctions being made by covering the ends with a cement box and filling up with asphalt. The current leads are of copper, those connecting the cells of circular cross-section and 3 cm. in diameter. They are all painted with a composition stable against chlorine and acid fumes, as are also the tin tubes and rubber connections referred to above. The cells are worked under slightly reduced pressure (1–2 cm. of water), and, as a matter of fact, no smell of chlorine was noticeable. Ventilation can be effected, if necessary, by blowing air in through the agency of a fan driven by a 10-h.p. motor. A travelling-crane is provided to facilitate lifting off the tops of cells, &c. Fig. 4 gives a general view of the cell-room.

Saturated brine is used, prepared in the simplest way. A long cement

* The patent rights are not there available.

trough is filled with large lumps (20–40 cm.) of crude salt. Water enters continuously at one end, and saturated brine leaves at the other. It is not purified, and can be sent straight to the cells. The average cathode liquors produced contain 12–13 per cent. NaOH and about 20 per cent. NaCl. By decreasing the rate of flow of brine, 16 per cent. NaOH can readily be made. Up to 350 litres of brine per cell are causticized in 24 hours. The liquors are first evaporated in two vacuum pans, furnished by the Skodawerke A.G., Pilsen, and similar to those used in sugar refineries. In these they are successively brought to 35° and 40° B. Then by means of a Kaufmann rapid evaporator they are brought to 50° B. before going to the melting-house. The final product, which will probably be later somewhat improved upon, contains 97 per cent. NaOH, 1·2 per cent. Na_2CO_3, and 1·8 per cent. NaCl. The chlorine is diluted with air and absorbed in milk of lime.

Cells which are worked at room temperature take about 4 volts. Those I saw working at 65–70° require 3·4–3·5 volts. Long-continued experiments carried out with a 250-ampere unit have shown that at the normal working temperature of 85° the voltage falls to 1·3 volts (*plus* in all cases the voltage drop in the leads). The cathodic current efficiency is about 92 per cent. for 3n–4n alkali.

It remains to be added that wear and tear in the cells are very small. Under normal working conditions the anodes lose about 1 mm. in thickness at their bottoms and sides in two months. Suspended matter in the brine settles on the bottom of the cells, and the asbestos hoods remain unaffected. Finally, when once matters are adjusted, the whole system works automatically. The actual cell-room in Gratwein is worked by shifts of one workman only, whose duty it is to adjust the rates of flow in the different cells. Moderate fluctuations in rate of flow of brine or in current density result in a change in the alkalinity of the liquors produced, and in a corresponding *small* change in current efficiency. The cells at Gratwein work at a current density between the electrodes of about 2 $\frac{\text{amps.}}{\text{d.m.}^2}$ only. With cells working at 85° the most convenient figure, according to Billiter, is 4–6 $\frac{\text{amps.}}{\text{d.m.}^2}$; but, by suitably varying the other conditions, 14 $\frac{\text{amps.}}{\text{d.m.}^2}$ can be employed.

The withdrawal of 350 litres of catholyte per cell per 24 hours corresponds to a movement of the brine of about 0·00007 $\frac{\text{cm.}}{\text{sec.}}$. The OH' ions in that part of the catholyte between the electrodes will have a velocity anodewards of just about the same magnitude. (*E.g.*, assuming the cell to work at room temperature, the conductivity of the electrolyte would be about 0·5 $\frac{\text{recip. ohm}}{\text{cm.}^3}$, the velocity of the OH' ion at a voltage gradient of 1 $\frac{\text{volt.}}{\text{cm.}}$, 0·0018 $\frac{\text{cm.}}{\text{sec.}}$, and the actual velocity $\frac{0{\cdot}02 \times 0{\cdot}0018}{0{\cdot}5} = 0{\cdot}000072$ $\frac{\text{cm.}}{\text{sec.}}$).* This close approximation between the two opposing velocities, with the consequent straying of OH' ions towards the anode, is of course the chief cause of the 8 per cent. deficiency in current efficiency, as the amount of chlorine which dissolves in the concentrated brine, and which would thus tend to be carried to the cathode, is very small.

The second installation of the Billiter membrane cell is at the present time being erected in Saxony.

* *Principles of Applied Electrochemistry*, p. 368.

In conclusion, I will again emphasize the chief characteristics of the Billiter-Leykam cell. They are—

(1) Freedom from diaphragm troubles.
(2) Use of impure brine.
(3) Automatic working, great adaptability, and low attendance charges.
(4) Alkali (3n–4n) strong compared with most other non-mercury cells.
(5) With heated cells, lowest energy consumption per ton of product of any cell now working on a large scale.
(6) Large floor space needed.

DISCUSSION.

Mr. Joh. Härdén asked whether there was any appreciable formation of carbonic acid in the cells. In a plant in which he had been interested the formation of carbonic acid was found to give some difficulty. Was there any trouble caused by the gas collecting under the anodes, because he noticed these were not perforated? Further, he would like to ask what was the voltage across the block, or group of cells, and he would also like to know whether any trouble was caused by the cement lining of the cells getting saturated with brine and carrying current, or was there a brine-proof glazing inside?

Mr. H. M. Ridge asked whether the sloping of the cathodes produced any noticeable unevenness of current, and if so whether this in any way affected the efficiency of the cells.

The Chairman, in thanking the author for the valuable detailed information he had been able to bring before the Society, asked whether the particulars of Billiter-Siemens plants had been supplied to the author. He also inquired whether there had been any corrosion in the ferro-concrete cells. The question had recently received considerable attention, and some experiments made in Vermont seemed to demonstrate that iron wholly embedded in concrete was liable to electrolytic corrosion even when not joined to any terminals. The cathode hoods used must in a certain sense act as filters and become clogged; how long could they be used? Did the anodes wear evenly over the surface and at the edges?

Dr. A. J. Allmand, in reply to Mr. Härdén, said the amount of carbonic acid formed was very small. This fact was intimately connected with the high cathodic current efficiency. The formation was of course greater with cells working at 85° than with those kept at lower temperatures. No trouble was caused by gas collecting under the anodes. The voltage given in the paper was the average for a whole series of cells. With regard to the lining of the cells, the top was lined with glazed earthenware bricks. The amount of current passing through the cell walls was infinitesimal, as the pores in the cement soon became filled with solid crystallized salt. The cells stood on glass insulators.

In reply to Mr. Ridge, no measurements had been made, but he did not think any noticeable effect resulted from the sloping of the cathodes.

In reply to Dr. Borns, the particulars of the Billiter-Siemens plants were in part taken from existing publications, in part supplied by Siemens and Halske, and in part by Dr. Billiter.

With regard to the wear of the cathode hoods, a two-months' continuous test with a 250-ampere unit had shown that no deterioration took place, and this was the six-months' experience of the plant at Gratwein. There was no *filtration*, as in the Billiter-Siemens cells, but merely *diffusion*. Sus-

pended particles were gently deposited on the tops of the hoods or on the bottom of the cell. Lime and iron salts were precipitated outside the hoods by alkali which had diffused outwards. The anodes, being of Acheson graphite, would wear quite evenly. A certain amount of fine dust settled at the bottom of the cells. He did not know anything about the disability of ferro-concrete, but he believed the designer (with his considerable experience) and the users of the cells had a good opinion of it.

NOTE ON THE ELECTROLYSIS OF NITRIC ACID SOLUTIONS OF COPPER.

By J. H. STANSBIE, B.Sc., F.I.C.

(*A Paper read before the Faraday Society, Tuesday, November 26, 1912, Dr. H. Borns in the Chair.*)

In the electrolytic deposition of copper from nitric acid solutions it is practically impossible to deposit the whole of the metal upon either a rotating or stationary cathode under ordinary conditions; and in considering the results of experiments in which a copper-coated cathode was caused to rotate in a nitric acid solution with no current passing, the probable cause of the failure of the current to deposit the last traces of copper from a nitric acid solution suggested itself.

The object of the preliminary experiments was to determine the difference in the rate of reaction of dilute nitric acid with copper at rest and in motion. For this purpose a platinum cathode was thickly coated with copper by electrolytic deposition. After drying and weighing it was rotated in 50 c.c. of nitric acid (sp. gr. 1·108) containing about 10 grams of HNO_3 and less than 0·1 mgr. of HNO_2. When the rotation was stopped the cathode was at once removed, washed, dried, and reweighed. It was then immersed in a similar solution, but was allowed to remain at rest for the same length of time. The beaker was immersed in a vessel containing water at room temperature. All the conditions were kept as constant as possible, except that the metal was rotating in the one case and at rest in the other. The following remarkable results were obtained :—

i.	Rotated for one hour,	weight of copper dissolved	=	6·5	mgr.
	Rest	"	=	780·6	"
ii.	Rotated for two hours	"	=	15·4	"
	Rest	"	=	3,486·3	"

It is well known, but often overlooked, that nitrous acid plays a very important part in the dissolution of copper in nitric acid, and that the lower acid, or nitrite, accumulates in the solution. In solutions containing only traces of nitrous acid the action is very slow at first, but gradually increases as more nitrite is formed. If this is allowed to remain on the surface of the metal the general reaction is rapidly accelerated, but if it is hurried away into the mass of the solution the reaction is retarded. This is the most obvious explanation of the results given above.

Now in the ordinary electrolysis of nitric acid solutions of copper the solution is boiled in the first instance to decompose nitrous acid and nitrite, and to expel the products of their decomposition; but nitric acid is again reduced to nitrous acid by the current during electrolysis, and all the conditions for the dissolution of copper from the cathode are present. At first the current deposits the metal very much faster than it is redissolved, but finally, when only traces of metal are present in the solution, dynamic

equilibrium is reached, and no further permanent deposition of the metal can take place. This furnishes another argument in favour of the rotating cathode over the stationary one when purely nitric acid solutions are used.

The following experiments were then made as a further test: 5 grams of electrolytic copper were dissolved in 50 c.c. of 1·2 nitric acid, and the solution evaporated to one-fifth its bulk to decompose nitrous compounds. It was then made up to 500 c.c., and the free nitric acid in 50 c.c. determined. This was found to be 236 mgr. The remaining solution was electrolysed with a rotating cathode in 50 c.c. lots. Additions of free acid were made as shown in the table, and the other conditions were kept as constant as possible. The measured volume with additions was made up to 100 c.c. in each case.

The potential difference between the terminal of the rotor carrying the cathode and the anode = 3·2 volts. Current = 1·5 amps. Duration of experiment = 40 minutes.

TABLE OF RESULTS.

	1.	2.	3.	4.
Experiment.	Weight of Copper Deposited.*	Free Nitric Acid Present.	Nitrous Acid Found.	Free Sulphuric Acid Present.
1	474·3	236	33·0	—
2	497·4	236	28·8	—
3	497·3	236	16·3	4,500
4	455·0	1,236	33·5	—
5	495·5	2,236	30·9	—
6	495·7	3,236	31·3	—
7	424·8	4,586	38·1	—
8	314·7	6,326	60·3	—
9	494·0	6,326	14·2	4,500

* Weights are expressed in milligrams.

It will be seen from the table that the more or less perfect deposition of the copper depends upon the concentration of nitric acid and of nitrous acid in the solution, the smaller deposit corresponding to the greater concentration of the higher acid, while for the same concentration of the "ic" acid the smaller deposit corresponds to the greater concentration of the "ous" acid. From experiments 5 and 6 it would appear that up to 3 grams of HNO_3 per 100 c.c. of solution the deposits are good providing the nitrite keeps low; but beyond that the deposit is poor.

Before the introduction of the rotating cathode the method adopted by the author was to evaporate the nitric acid solution with sulphuric acid before electrolysis, as it was found impossible to deposit the whole of the metal without getting rid of the nitric acid, on account of the low current density used. But with the rotating cathode it is sufficient to keep the nitric acid low and add from 2 to 3 c.c. of strong sulphuric acid. The usual plan is to dissolve about ·5 gram of the metal in 10 c.c. of 1·2 nitric acid, boil down to decompose nitrites, and make up to 100 c.c. with addition of 2 c.c. of concentrated sulphuric acid. After 40 minutes' electrolysis the exhausted solution will very rarely give any coloration with sulphuretted hydrogen. To prevent any re-solution of the metal when the circuit is broken the following simple plan has been found very effective: a wash-bottle with a long rubber tube

attached to the mouthpiece is arranged so that when the rotation is stopped a jet of water can be directed upon the cathode, while the current is gradually broken by lowering the beaker. The fixed wash-bottle with the flexible tube allows the operator to use both hands in manipulating the apparatus.

The action of the sulphuric acid is probably twofold : (*a*) its ions help to carry the current and thereby to check the formation of nitrous acid ; (*b*) it unites with nitrous acid to form a nitro compound which is much less effective in bringing about re-solution of the metal. Comparison of the results of experiments 2, 3, and 8, 9 makes the first part of this explanation clear. The second part was suggested by the late Dr. Edward Divers in discussing the results of some experiments on the reactions of metals and alloys with nitric acid, which the author had carried out.

METALLURGICAL LABORATORY,
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A NEUTRAL OIL EMULSION AS A MODEL OF A SUSPENSION COLLOID.

By RIDSDALE ELLIS, B.Sc.

(*A Paper read before the Faraday Society, Tuesday, November 26, 1912, Dr. H. Borns in the Chair.*)

This work was taken in hand with a view to obtaining some quantitative data on the relations between the electrical charge carried by the particles of an emulsion, the surface tension on the oil-water interface, and the phenomenon of coagulation, with a view to throwing light on some of the phenomena of colloidal solutions.

The influence of electrolytes on emulsions has been studied by Hatschek,* who used emulsions in which the dispersed phase was the same specific gravity as the continuous phase. In this case, when electrolytes were added, coalescence of the particles took place whenever the Brownian movement brought the globules into contact. As the effect of gravity was eliminated, the increase in size ceased when the Brownian movement became too slight to bring the globules into contact.

The present work was undertaken largely with a view to ascertaining under what conditions this coalescence takes place with the greatest rapidity. The phenomenon of coalescence or coagulation is largely an electrical one, so that the problem involved is to measure with more or less accuracy the changes in the interface potential which occur when electrolytes and other coagulants are added, and also to measure under the same conditions the changes in the tension at the surface of the particles in question. With regard to the first of these two requisites, the principal trouble in the way of determining the interface potential at the surface of the particles of colloidal solution is the readiness with which coagulation takes place. It is hard, for instance, to get Hardy's iso-electric point, since the coagulation occurs before the sign of the charge has been reversed.

By the use of emulsions, especially oil emulsions, this trouble can be overcome. Oil emulsions have also the advantage that the surface tension between the oil and the medium in which it is suspended can be easily determined for approximately flat surfaces of large radius of curvature. Finally, the size of an oil globule suspended in another fluid probably depends more completely on its electrical charge and the tension at its surface than is the case with suspensions or colloidal solutions of solids.

The method employed for measuring the interface potential at the surface of the oil globules has been already fully described by the author,† and will be only briefly referred to here. The usual way of determining the migration velocity of a colloid in solution has been by means of a U-tube, in which the lower part of the tube is filled with water and the emulsion or the like placed on top in either arm. The rate of movement of the boundary under the influence of an electrical field is then observed. If, however, such an

* *Zeitschrift für Kolloide*, 9, 159, 1911.
† *Zeitschrift für Phys. Chemie*, 78, 3, 321, 1911.

apparatus is employed, the effect produced is illustrated diagrammatically in Fig. 1. The conical shape assumed by the boundaries is due to the fact that the water at the surface of the glass walls of the tube moves relatively to the glass under the influence of the electric potential just as the particles of the emulsion move through the body of the water. In this way a circulation of the water is produced in the directions shown by the arrows. In view of this, a microscopic apparatus was employed, comprising a flat layer of liquid between two glass plates provided with electrodes near their ends, so that by a process of integration of the observed velocities at all depths between the two glass surfaces the true velocity of the oil globules relative to the water was determined.

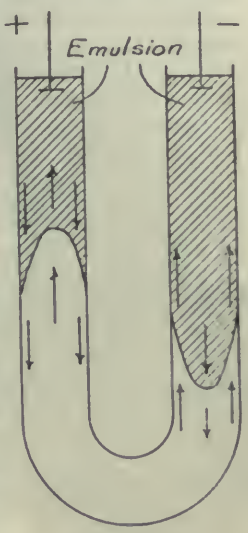


FIG. 1.

The interface potential at the oil-water surface was calculated by means of Helmholtz's well-known formula from the figures obtained for the migration velocity of the oil globules under unit potential gradient. This formula, of course, involves the dielectric constant of the medium in which the particle is suspended; and although this has been accurately determined for pure water, it changes very considerably for electrolytes, which tend to largely increase the value of this constant. It is convenient, however, to express the results in terms of the interface potential rather than the migration velocity, because this enables the results obtained to be compared with electrolytic and other potentials existing at solid-liquid or liquid-liquid interfaces.

Emulsion of	Volts at Surface of Oil.	Volts at Surface of Glass.
Special acid-free oil...	0·050	0·064
	0·053	0·057
Acid-free oil	0·045	0·037
Kahlbaum's liquid paraffin... ...	0·040	0·040
Cylinder oil (3 per cent. woolgrease)	0·050	0·013
Water-soluble oil	0·066	0·040
Aniline (redistilled)	0·043	0·060
Chloroform	0·014	0·041
Gamboge	0·025	0·035
Gum mastic	0·024	0·020

The interface potential at the surface of an emulsion made with pure CO_2-free water and a practically acid-free hydrocarbon oil was found to be 0·053 volts. This potential was found to be of the same order of magnitude as that at the surface of impure oils and other substances (see Table), and also agrees well with the figures herewith obtained by Whitney and Blake, Gee, and others for gold sols and other true colloidal solutions. The pure oils in particular are seen to be strongly negatively charged in what must be nearly neutral solution, which is in agreement with Coehn's empirical law,* which states that where two substances are in contact, the one having the higher dielectric constant will be positively charged and the other negatively.

* *Ann. Phys.*, 3, 4, 217, 1898.

Further, the results appear to show that the presence in the oil of comparatively large amounts of organic impurities, such as woolgrease, does not appear to greatly affect the order of magnitude of the potential. Also, if the chemical nature of the emulsified substance were of essential importance, it would be expected that aniline, being a base, would be positively charged; whilst chloroform, not possessing basic character, would be negatively charged as usual, or at least that the negative charge would be less in the case of aniline than of chloroform. The reverse was found to be the case.

Great precautions were not taken to free the emulsion from all electrolytes, so that the nature of the charge in the absence of electrolytes cannot be dealt with here. However, the object of this Paper is to study the action of elec-

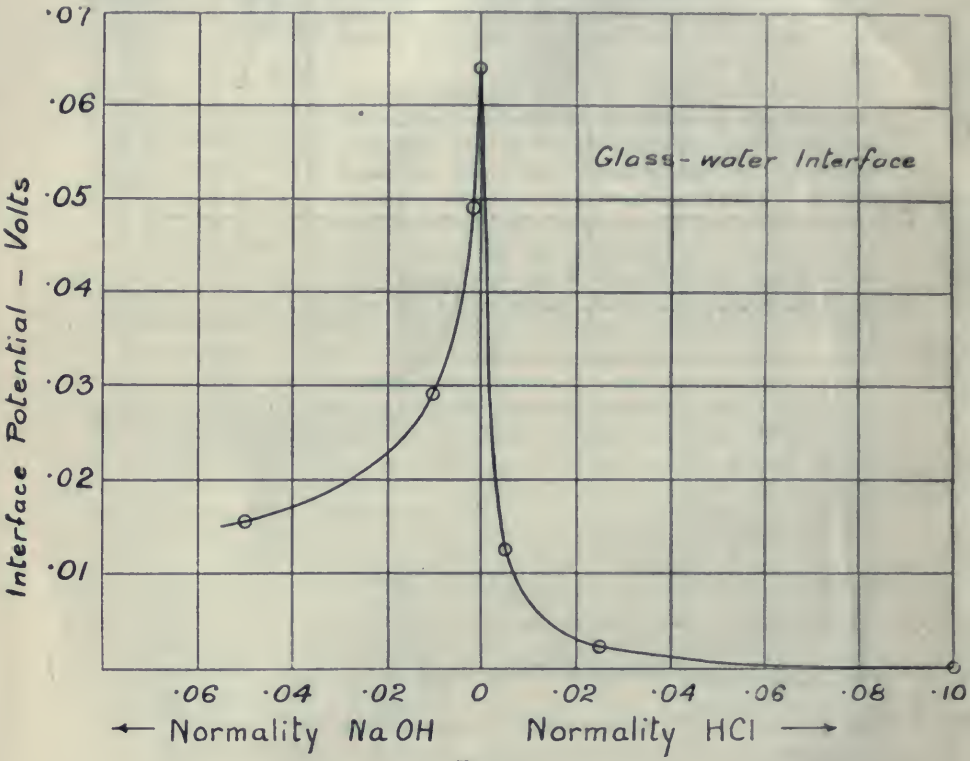


FIG. 3.

trolytes in such concentrations that the effect of such slight amounts of electrolytes as may be present initially is entirely swamped. It is of course well known that hydrogen and hydroxyl ions have a relatively enormous influence on colloidal phenomena, and the effect of acids and alkalies on the interface potential of an oil emulsion was next examined. The results are shown in Figs. 3 and 4. The interesting point here is the maximum point obtained in neutral or slightly alkaline solutions. Perrin's* data obtained by electrocapillary experiments show entirely different results (see Fig. 5), which are not confirmed by coagulation results, as will be seen later. From the present results it also appears that in the case of a substance which does not react with acid or alkali to form a complex ion such as occurs with albumen, globulin, etc., the maximum interface potential is either at the

* *Journ. de Chim. Phys.*, **2**, 601, 1904.

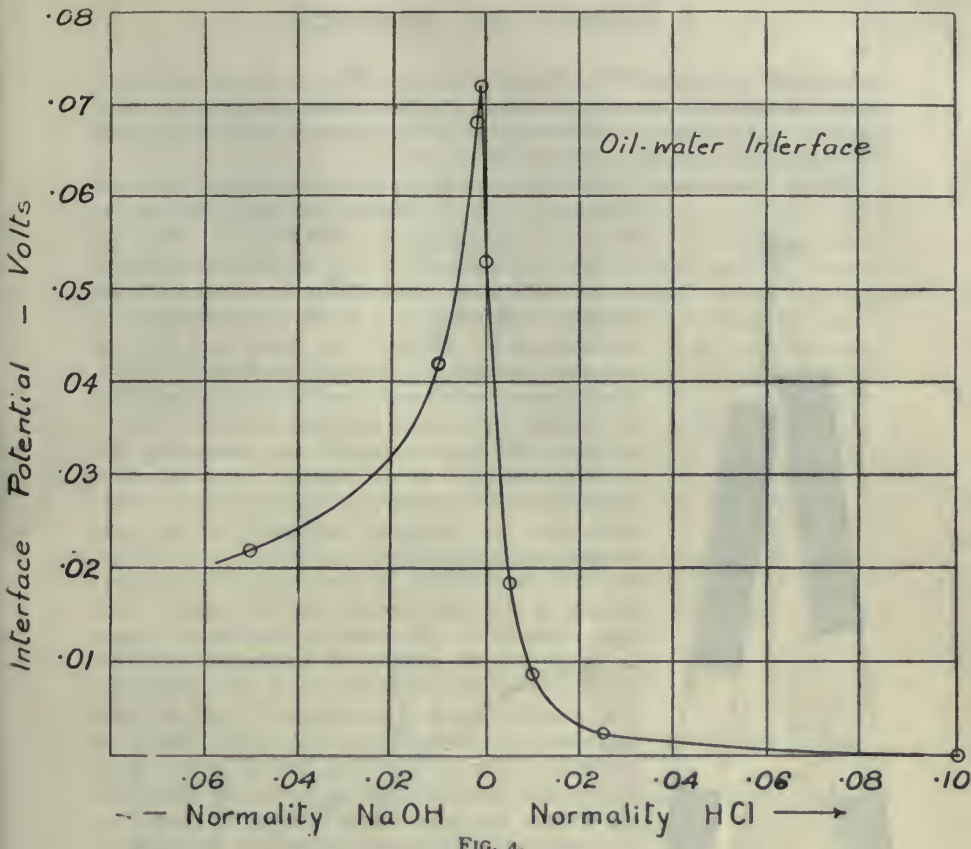

·08
·07
·06
·05
04
·03
·02
·01
Interface Potential – Volts
Oil-water Interface
·06 ·04 ·02 0 ·02 ·04 ·06 ·08 ·10
– – Normality NaOH
Normality HCl →

FIG. 4.

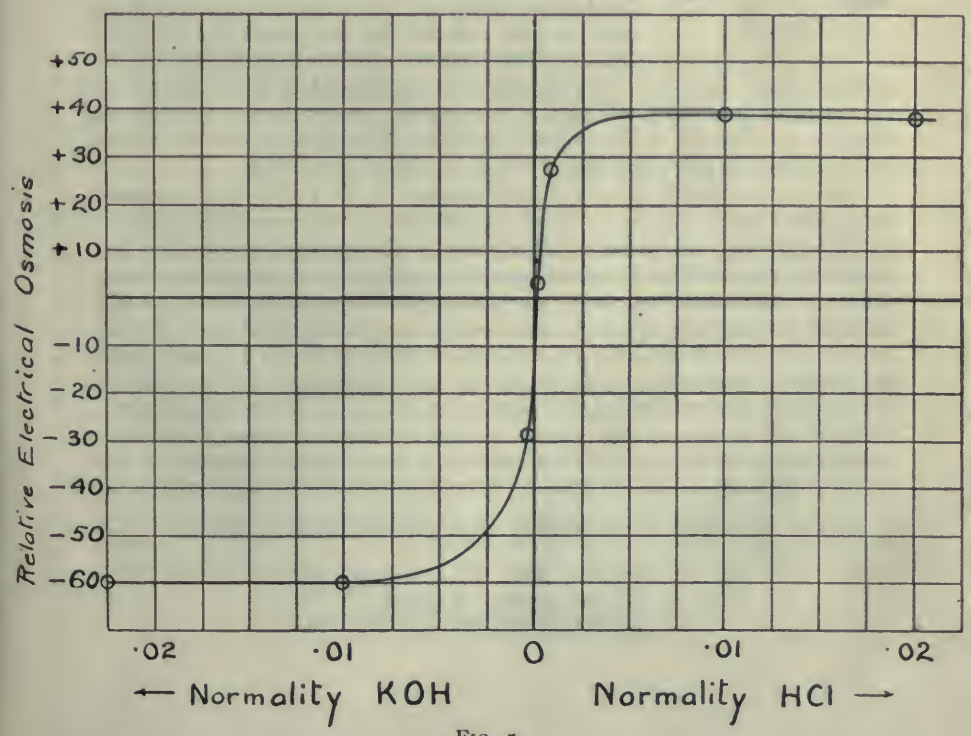

+50
+40
+30
+20
+10
–10
–20
–30
–40
–50
–60
Relative Electrical Osmosis
·02 ·01 0 ·01 ·02
← Normality KOH
Normality HCl →

FIG. 5.

neutral point or in very dilute alkaline solutions. The position of this maximum is confirmed moreover by the observations on the stability of other emulsions and colloidal solutions made by Whitney and Straw,* Bredig,† and other experimenters. This will be referred to later.

Having determined the interface potential and the change produced therein by acids or alkalies, the next step was to see what effect these substances had on the stability of the emulsion and to try to co-ordinate these results with those obtained for the changes in the interface potential. To do this, the samples of emulsion were allowed to stand and then a measured amount of emulsion was drawn off from the bottom of each sample and its turbidity as compared with the original emulsion measured quantitatively. The apparatus used for comparing the relative turbidities of two samples consisted of a simplified form of Richard's nephelometer.‡ This instrument was designed originally for the comparison and estimation of opalescent precipitates, and its use depends on the amount of light reflected by the solid particles in the liquid. The light reflected by the matter in suspension is proportional to the amount of suspended material, provided that the particles are of the same size. The simplified form of nephelometer used for these experiments is illustrated in Fig. 6, and consists of two test-tubes with their rims cut off so that black sleeves can be readily slid up and down the tubes, the ends of the tubes being covered or blacked so as to prevent any reflections from their curved ends. On looking down the black sleeve into the liquid only the light reflected by the particles in the liquid is seen. The relative turbidity is then obtained by sliding up and down the black sleeves until the amount of light reflected or the apparent turbidity is the same in both tubes. The standard of comparison consists of a sample of the original emulsion thoroughly shaken up before being placed in the nephelometer, and this is taken as unity.

FIG. 6.

This apparatus only gives a rough measure of the turbidity, its accuracy being about ± 10 per cent., but this is sufficient for the purpose in question.

In addition to determining the stability of the emulsion in the way described, the equilibrium size of particles in solutions of various concentrations was determined by taking 10 c.c. samples of emulsion, adding 10 c.c. of solutions of various concentrations to each sample and shaking for a week. At the end of that time the average radius of the particles in some of the samples was determined microscopically and the radius of the particles in the remainder interpolated or extrapolated by the help of the nephelometer. Further, the tension at the oil-water surface was determined. All these results are given in Fig. 7. The curve for the relative turbidity or the stability of an emulsion with different concentrations of acid and alkali shows a marked maximum corresponding to a concentration of alkali of $\frac{N}{1000}$.

* *Journ. Amer. Chem. Soc.*, 29, 325.
† "Anorganische Fermente."
‡ *Amer. Chem. Journ.*, 31, 325, 1904.

The existence of such a maximum point in dilute alkaline solutions between ·0002 N and ·001 N NaOH has been observed already by Whitney and Straw, Bredigand others in the case of coarse emulsions of turpentine, carvene, and also gold and platinum sols. The cause of this fact appears to be the increase in the interface potential due to the addition of small amounts of alkali. In fact, the stability appears, so far as the present experiments are concerned, to be rigidly dependent on the interface potential. The relationship between stability and interface potential and the iso-electric point has been discussed by a number of experimenters. Thus Burton* measured the change in the electrical charge carried by colloidal silver when varying amounts of aluminium sulphate were added, and noticed that in the neighbourhood of the iso-electric point the stability was less than when the interface potential was greater.

Now, in a colloidal solution or fine suspension the particles are all in rapid vibration on account of their Brownian movement, and will come into contact

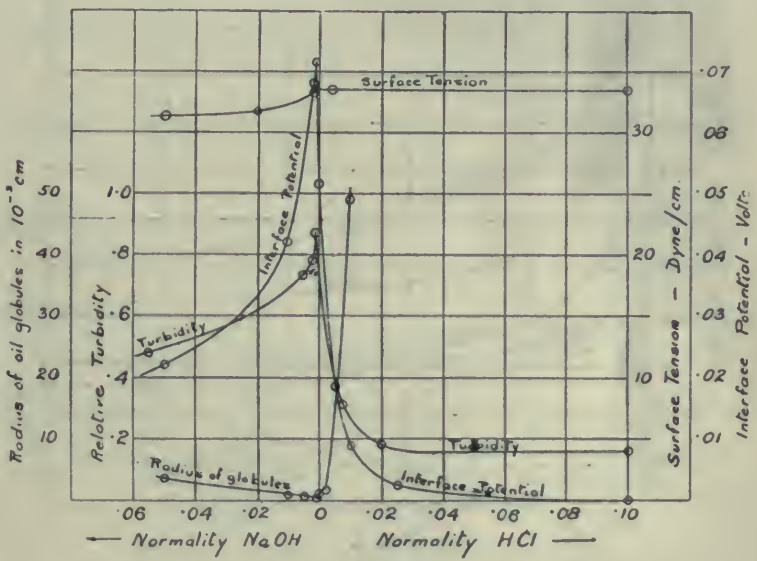


FIG. 7.

with each other repeatedly. If the solution is stable, the particles will not unite or coalesce in any way and will simply rebound or slide past each other. The key to the phenomenon of colloidal precipitation is the reason why these particles should unite with each other under some conditions and not under others.

Perrin† has shown that the particles of an emulsion tend to distribute themselves in a solution in accordance with the gas laws and that there is no evidence of mutual electrical repulsion, which has been given as the explanation of the stability of suspensions and colloidal solutions. The present results also go to show that Bredig's theory of colloidal coagulation based on surface tension changes is quite erroneous, at least as far as oil emulsions are concerned. The results obtained in the present work indicate that the rate of coagulation does not depend on the surface tension but on the electrical

* *Phil. Mag.* (4), **12**, 472, 1906.
† *Comptes Rendus*, 146, 967, 1908.

potential at the surface of the particles. Thus the surface tension of the oil against hydrochloric acid of increasing strength was measured and was found not to vary within the limits of experimental error, whilst the stability was decreased enormously by the same addition of acid. The globules have no mutual electrical repulsion on account of the layer of ions necessarily associated with the charge of opposite sign on the globules, which make the latter act as spherical condensers rather than as isolated charged spheres. It appears, therefore, that a true explanation of the results obtained is that suggested by Professor F. G. Donnan, namely, that the presence of an electrical double layer around the particles prevents them from coming into sufficiently close contact unless the kinetic energy of the collision of two particles is sufficient to enable the electrical double layer to be disrupted, and the less chance there will be that two particles colliding with one another will coalesce

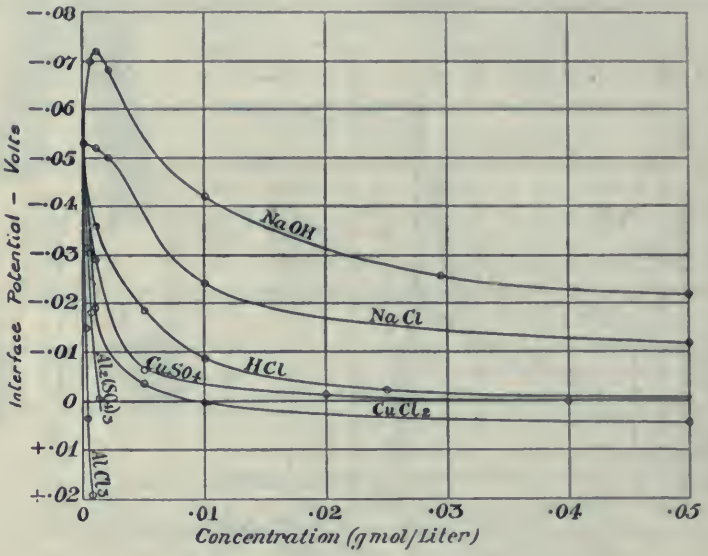


FIG. 8.

or adhere to each other. Strong confirmation of this view is given by the data obtained in connection with the iso-electric point. According to the above theory, when the charge is zero there is no opposition to the force tending to produce coalescence or aggregation, so that in the case of a colloidal solution in which all the particles are in rapid movement or vibration coagulation will occur extremely rapidly. Moreover, all the results obtained point to the fact that the globules of oil in an emulsion and the particles in a true colloidal solution are similar in their electrical properties.

Indirect evidence that coagulation occurs at the iso-electric point is given by the ratio of concentrations of salts with tri-, di-, and mono-valent kations required to just neutralize the charge on the oil globules. The contact-potential curves are given in Figs. 8 and 9. These concentrations approximate to a geometrical series, which agrees well with the similar series obtained by Schultze* and Linder and Picton† in connexion with the

* *Journ. f. Prakt. Chem.*, 26, 431, 1882.
† *Journ. Chem. Soc.*, 67, 63, 1895.

coagulation of colloidal solutions. In the latter case, the concentrations were those which were required to coagulate practically instantaneously the colloidal solution in question. The geometrical series obtained in the present case by determining the iso-electric point using chlorides of tri-, di-, and mono-valent salts was found to be—

1 : 39 : : 1,521,

while Schultze, also using chlorides, obtained from his coagulation experiments the corresponding series—

1 : 40 : : 1,600.

It must be observed in connexion with the series obtained by determining

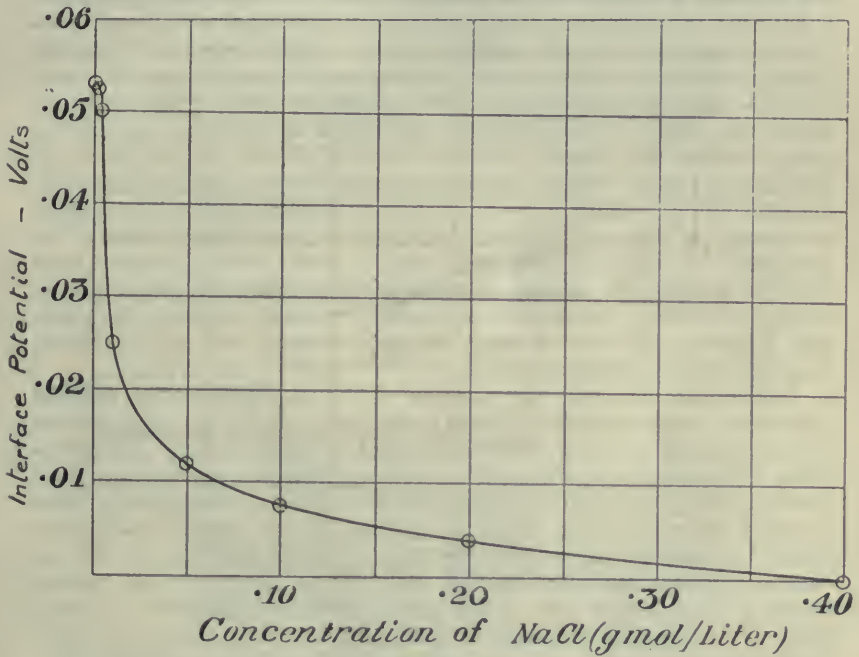


FIG. 9.

the iso-electric point of the emulsion that the existence of such a close agreement between these sets of ratios depends on the fact that the point at which the concentration is measured is the one at which the charge is exactly zero. Thus, if the points taken on the curve are those corresponding to a reduction of the electrical potential by 90 per cent. only instead of 100 per cent., the corresponding series becomes—

1 : 18 : : 730.

This series does not agree in the least with that obtained in connection with the coagulation of colloidal solutions. Hence, the evidence is very strong that the geometrical series obtained by Schultze, Linder, and Picton corresponds to the concentrations required to reduce the charge to zero and thus to eliminate all forces opposing coagulation, so that the solutions coagulate almost instantaneously. Further confirmation of this theory is

given by the results of Whitney and Ober,* who found that the amounts of various metals dragged down by the coagulation of a definite amount of negative colloid are in the ratio of their equivalent weights, and that for any given metallic salt the weight of the metal carried down is proportional to the quantity of the colloid, and is not dependent on the concentration of the salt of the metal. It was on the assumption that the above relationships were true that Whetham † evolved his mathematical explanation of the results obtained by Schulzte and others.

Of course, it must be borne in mind that the above results are only obtained in the case of substances which do not react chemically with the medium in which they exist or with the electrolytes which are added. They also do not apply to cases where a protective colloid surrounds the particles of the colloidal solution. Where chemical action occurs, entirely different phenomena are observed. For instance, colloidal solutions of such substances as albumen are only stable in alkaline or acid liquids and coagulate when the solution is made neutral. In these cases electrolytes are necessary to enable these substances to go into colloidal solution. These facts are exactly the reverse of those observed with neutral oil emulsions, and are due to the fact that the colloidal substances interact with the acids or alkalies to form colloidal salts. These salts then dissociate so that the radicle containing the globulin or albumen migrates as an ion. Stable solutions of albumen or globulin are obtained with both acid and alkali, since these substances are amphoteric. Noyes ‡ has also shown that a similar action probably takes place in the case of colloidal solutions of ferric hydroxide, silicic acid or simular substances. For example, aggregates of ferric hydroxide molecules may dissociate into one or more ordinary hydroxyl ions and a residual positively charged colloidal kation.

I have just considered the question of the coagulation of a colloidal solution by means of electrolytes, and I now wish to deal with the phenomena of the coagulation of one colloid by another of opposite sign. The phenomena of the mutual coagulation of two positively charged colloids have been investigated by Biltz, who found that within wide limits complete coagulation occurred, but outside those limits no coagulation took place.§ Biltz determined his limits of coagulation by mixing various quantities of the two colloids together, allowing them to stand for an hour and then making ordinary visual comparisons of the extent to which coagulation had taken place. It was found, however, in dealing with oil emulsions that a more rapid and more accurate method of determining these limits was to take 10 c.c. of emulsion, and add a colloidal solution of ferric hydroxide drop by drop, warming the solution meanwhile until coagulation occurs. This gives the lower limit. The upper limit is determined by taking 5 c.c. of colloidal ferric hydroxide and adding the emulsion gradually until coagula appear. The results obtained in this way were checked by allowing various mixtures of emulsion and colloidal ferric hydroxide to stand for two or three days and observing the extent to which coagulation had taken place. With the latter method, where necessary, the degree of coagulation was measured by filtering the emulsion and comparing in the nephelometer the amount of oil in the filtrate with that in the original emulsion. Simultaneously with these experiments the change in contact potential with various concentrations of ferric hydroxide was determined. All the results are given in Fig. 10. Now Ramsden ‖ has observed that colloidal ferric hydroxide solutions show intense

* *Journ. Amer. Chem. Soc.*, **23**, 842, 1901. † *Phil. Mag.* (5), **48**, 474, 1899.
‡ *Journ. Amer. Chem. Soc.*, **27**, 85. § *Ber.*, **37**, 1,095, 1904.
‖ *Proc. Roy. Soc.*, 72, 156, 1903.

superficial viscosity, indicating that a thin layer of ferric hydroxide separates out at the surface. Further, Pickering has shown that colloidal ferric hydroxide will act as an emulsifying agent.* Now Donnan and Potts found that those soaps which possess the power of emulsifying a neutral oil have concentrations at the oil surface far exceeding their ordinary solubility. In other words, a solid or semi-solid layer is formed. There is therefore every reason to suppose that the first action of the colloidal ferric hydroxide is to form a solid or semi-solid layer of ferric hydroxide around the globules. This layer will prevent coalescence, so that coagulation must be due wholly to the sticking together of the oil globules by means of ferric hydroxide precipitated between the globules of oil. The presence of such a precipitate around or between the globules is not visible under a microscope, as ferric hydroxide is too transparent to colour the oil globules of even the coagula, unless the latter are of considerable thickness. However, that such precipitation between the globules must take place is shown by the fact that the coagula produced are heavier than water and sink to the bottom, whilst the oil

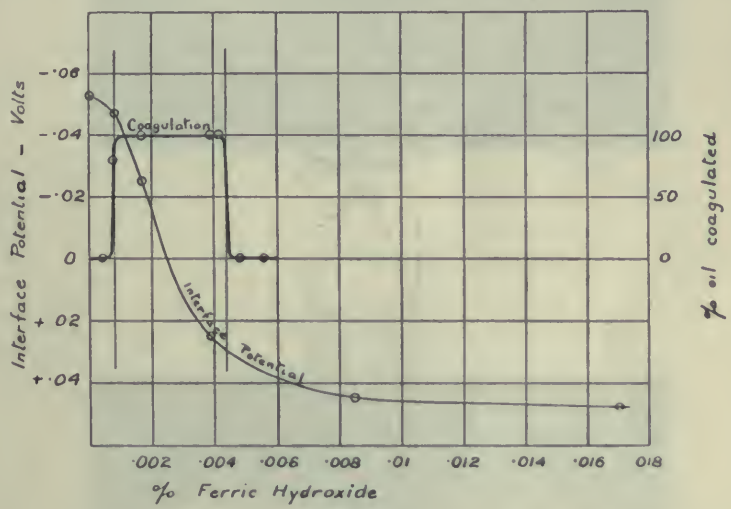


FIG. 10.

globules in ferric hydroxide solutions too concentrated to produce coagulation rise to the surface and form a white ring around the edge of the meniscus. Now, from the measurements made of the electrical charge on the individual globules, the electrically adsorbed layer of ferric hydroxide must be steadily increasing in thickness as its concentration in the solution increases. Hence, when coagulation occurs there must be deposited on the globules, in addition to the ferric hydroxide layer produced by electrical adsorption, an additional amount sufficient to weigh down the globules until they sink. This additional amount must necessarily be deposited between the adhering globules, as the deposition of ferric hydroxide on the exposed parts of the globules in the coagulation can only depend on electrical adsorption as in the case of individual globules.

This precipitation between the globules can be explained on the assumption that colloidal ferric hydroxide, like water vapour, will tend to precipitate on all surfaces having a small radius of negative curvature in preference to a

* *Journ. Chem. Soc.*, 91, 2001, 1907.

larger radius of negative curvature, and still more so to those surfaces having a positive curvature.

These factors may be too slight to produce the phenomena in question, but the following theory which is based on them is put forward tentatively as it explains all the facts, although it must be admitted there is no very conclus ve evidence to support it.

According to this theory, when two oil particles come into contact there is formed at the point of contact the equivalent of a surface of negative curvature with a very small radius on which $Fe(OH)_3$ will very readily precipitate, thereby uniting the two particles together (see Fig. 11). This precipitation will not occur until the amount of the $Fe(OH)_3$ is sufficient to produce in the short space of time the particles are in contact a bond sufficiently strong to

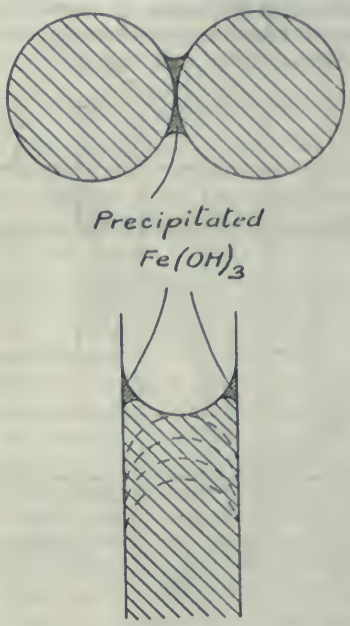


FIG. 11.

prevent the globules separating again by Brownian movement. When the globules are united in pairs, others will be joined to them in exactly similar manner until all the oil globules are held together in large coagula cemented by ferric hydroxide.

The existence of an upper limit of concentration above which coagulation does not take place can be readily explained by the presence of an electrical double layer around the globules of the same sign as that around the particles of colloidal $Fe(OH)_3$. When the positive contact potential has increased to a sufficient extent, the electrical double layer, as already explained, will be sufficiently strong to prevent the deposition of ferric hydroxide, except under very favourable conditions. When these conditions do not occur often enough to allow, during the time of contact of two particles, a sufficient amount of ferric hydroxide to be precipitated to prevent the globules separating again by Brownian motion, coagulation cannot take place. This will not prevent a slight further precipitation of ferric hydroxide on the oil surface, as in this

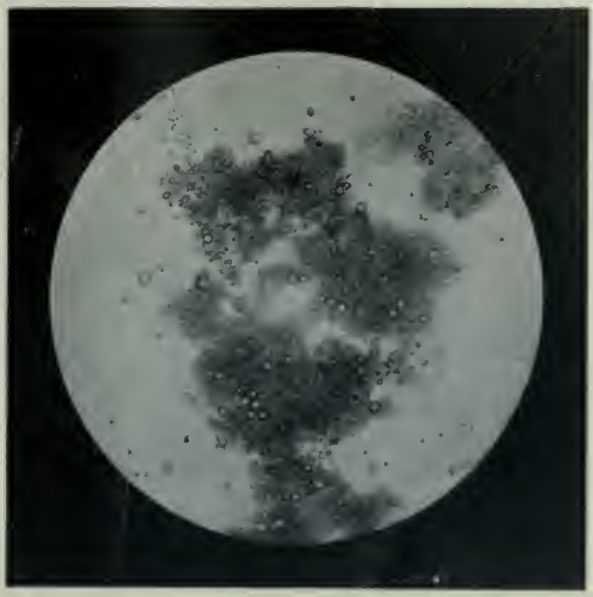


FIG. 12.

FIG. 13.

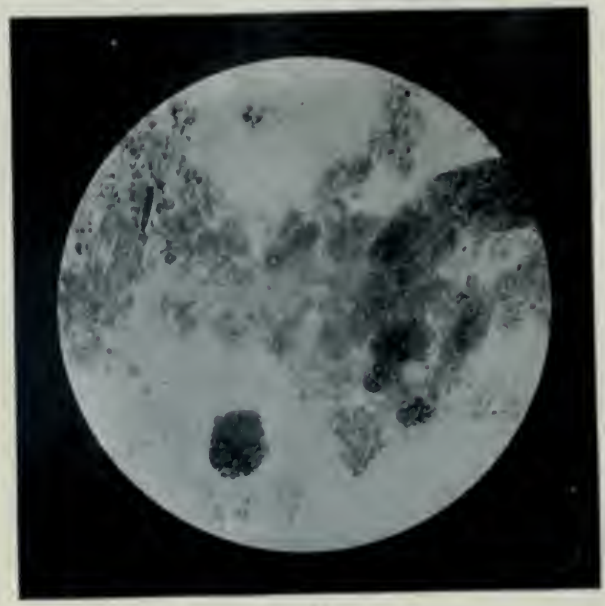


FIG. 14.

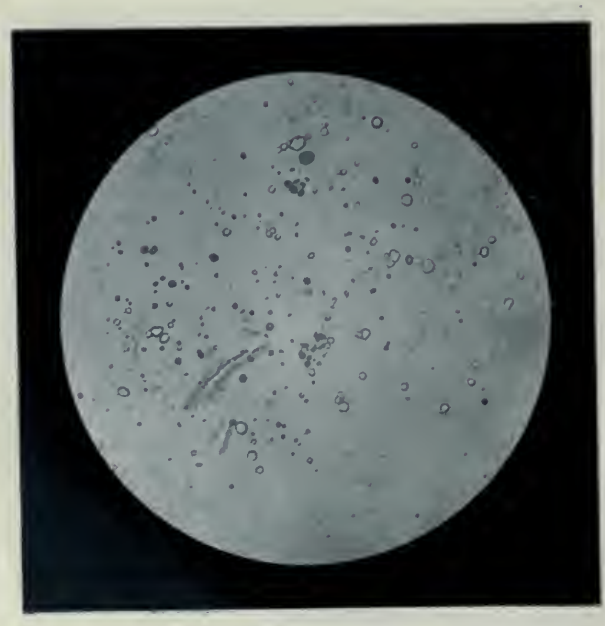


FIG. 15.

case there is no such time limit within which a certain minimum precipitation must occur.

Exactly similar conditions are present when the well-known phenomenon of capillary coagulation of positive colloids occurs in negatively charged capillaries. In this case the surface of negative radius of curvature is found in the corner between the glass-water and the air-water surfaces. That precipitation of colloidal ferric hydroxide does actually take place at this part can be observed microscopically. If the capillary is not excessively fine the coagulation is limited to this corner, but where the tube is thinner coagulation can continue along the tube (as indicated in dotted lines in the figure), provided that the radius of curvature of the surface of the precipitate formed in the tube is small enough to induce precipitation. In the former case the capillary flow of the liquid is little impeded, but in the latter, as in the case of a filter-paper, the flow of liquid is stopped owing to the blocking of the capillaries with the coagulated colloid.

Fichter and Sahlbom * explained this capillary precipitation as the result of the electromotive forces produced by the liquid flowing up the capillary. However, in the case of a colloidal globule such an electromotive force cannot be produced, as the only movements of the liquid and the particle relative to each other are the extremely slight movements due to gravity and that due to the Brownian movement, neither of which can produce anything approaching the voltage required by this theory. Hence, some other theory such as that just given must be put forward to account for the coagulation of one colloid by another.

It is possible that dyeing may be due to some such capillary coagulation of the colloidal dye in the pores of the material. A discussion of this question is, however, beyond the limits of this Paper.

The factors producing these phenomena with oil emulsions and ferric hydroxide do not appear to be limited to those cases where two oppositely charged colloids or suspensions are mixed. For instance, exactly similar coagula are formed when a basic salt is precipitated in the emulsion as the result of a purely chemical or electrolytic action. Figs. 12, 13, and 14 are photomicrographs of coagula produced respectively by electrolytically forming basic ferrous carbonate in the emulsion, by adding colloidal ferric hydroxide, and by precipitating basic ferrous sulphate in the emulsion. It appears necessary that a basic salt akin to the positive basic colloids should be formed, as Fig. 15 shows that the result of the precipitation of aluminium silicate in the emulsion is merely mechanically to include the particles and not to bind them together in clumps. The purification of water from suspended and colloidal matter by precipitating substances therein is certainly due to some such binding-together action on the suspended particles as has been discussed in connection with oil emulsions. Probably in all these cases the radius of curvature of the surface available for precipitation plays a very important part.

I take this opportunity of expressing my thanks to Professor Donnan for his help and the many suggestions he has made during the course of this work.

Muspratt Laboratory of Physical and Electrochemistry
June, 1912.

* *Verh. d. Natur. Ges. in Basel*, **21**, 1, 1910.

DISCUSSION.

Professor F. G. Donnan, F.R.S. (*communicated*): Mr. Ellis has given the members of the Faraday Society an excellent, though necessarily brief, survey of the work which he has been carrying out under my direction for the last two years on the subject of pure oil emulsions. We see that no distinction can be made between "suspensoids" and "emulsoids," if based merely on the liquid or solid state of the disperse medium, as has been attempted by some authors. For the oil emulsions investigated by Mr. Ellis behave as typical suspensoids; so that indeed such pure "mechanical" oil emulsions form a very striking model of a "suspension colloid."

It is also clear that Bredig's "Lippmann Effect" theory of the stability of suspensoids is not borne out by the results obtained by Mr. Ellis. This is shown by a comparison of the contact-potential, stability, and interface-tension measurements.

In conclusion I may mention that further work on emulsions is at present being carried out in various directions in the Muspratt Laboratory.

Mr. Emil Hatschek thought Mr. Ellis had correctly described the emulsions dealt with in his Paper as "models" of suspension colloids, inasmuch as that title was generally applied to reproductions differing considerably in size from the objects represented. He understood that the size of the initial oil globules was about $2\,\mu$, and such a system was coarse compared even with many ordinary precipitates, and still more with real suspensoids, which began about the limit of microscopic visibility, say about $0{\cdot}4\,\mu$. As Mr. Ellis had chiefly considered properties more or less independent of the size of the particles, such as contact-potential, the point was not vital, but it could not be disregarded in considering the stability. This seemed to him a very ill-defined quality, especially in a system which was unstable from the outset: an emulsion with particles of that size would clear in a short time, simply under the influence of gravity. He also had great doubts as to the accuracy of the nephelometer, as it appeared to him unlikely that light from all particles, except at enormous dilutions, could reach the eye. He considered the only conclusive method, no doubt much more laborious, microscopic measurements and counts, which were fairly easy with particles of this size.

As regards the reason suggested for the absence of collision between the particles while still charged, viz., the double layer, he always found great difficulties in dealing with this conception; while he understood that energy was required to shear the double layer, he could not understand why it should prevent collision if the particles with the layer were looked upon as condensers. The point brought out by the Paper, viz., that the maximum charge and stability occurred in neutral or slightly alkaline solution, appeared to him deserving of attention.

With reference to the action of ferric hydroxide as a positive colloid, he found some difficulty in accepting the suggested theory, which made the sign and magnitude of the radius of curvature the determining factor. In the capillary coagulation of ferric hydrate, the latter was undoubtedly deposited not only in the meniscus, but on the whole surface of the glass. He had also found in experiments described in 1910 that ferric hydrate in the gel condition, *i.e.*, already precipitated on large surfaces like those of wood-wool, took oil globules out of condense water, and he was inclined to believe in a purely mechanical action.

He had always advocated the study of oil-water emulsions, as they were

the only systems which could be obtained free from electrolytes, and he hoped Mr. Ellis might extend his investigations to such emulsions, prepared with due precautions, which might perhaps help to throw light on the question—still obscure—of the origin of the charge on suspensoid particles.

Professor A. W. Porter, F.R.S.: I wish first to congratulate the author of the Paper on having raised so many interesting points. I do not feel altogether in agreement with the criticisms made by Mr. Hatschek. For example, I do not share his lack of enthusiasm for the electric double layer. No doubt the mechanism of this layer is not immediately obvious. A perfectly uniformly charged double layer would, of course, be a self-contained system irresponsive to external electric fields. The fact that suspensoids drift in an electric field demonstrates, however, that the charges cannot be uniformly distributed. In such a case there may be an action between neighbouring particles, and this will be a repulsion, as is supposed in the Paper.

Mr. Hatschek has some doubt about the validity of Whetham's conclusions in regard to the numbers obtained for the precipitating power of mono-, di-, and tri-valent ions respectively. I do not think that taking the suspended particle as fixed will have any serious effect on the values calculated theoretically. A similar problem turns up in the kinetic theory of gases, and in that case no serious change is required when the movement of a particle is recognized.

With regard to the meaning of the results obtained with the nephelometer, Mr. Hatschek's criticisms seems to be more just. Even for large and uniformly sized particles the interpretation of the results can only be simple when the particles are so sparsely distributed that the light reflected from any one can reach the eye without having been intercepted by intervening particles. I should like to learn, however, from the author, more details with regard to the size and density of distribution of the particles in his experiments, in order that one may judge as to how far this criticism is valid.

Dr. E. Feilmann remarked that the fact that slightly alkaline media favoured the production of stable suspensions, of colloidal character and otherwise, had long been known, and was supported by much experimental work by Wottermoser and others. He himself had observed the fact repeatedly in the case of colloidal suspensions of tungsten and similar substances, and had been inclined to attribute it to the removal of surface layers of oxide from the metallic particles, but the same action took place in cases where no oxide could form. Further, in some cases slightly acid solutions helped the stability of the suspension, as in the case of colloidal zirconium.

Dr. G. Senter said the theory that the particles in a colloidal solution were kept from coming into actual contact by the presence of an electrical double layer unless the kinetic energy of collision was sufficiently great to cause the rupture of the layer was very interesting, but required more detailed statement. The suggestion that a particle with such a double layer could be regarded as a closed system without any electrical effect towards the outside appeared improbable for several reasons.

He agreed with Professor Donnan that Mr. Ellis's results appeared to do away with any real distinction between suspension and emulsion colloids, and rendered necessary a reconsideration of the classification of colloidal systems. This view was supported by the recent results with colloidal sulphur obtained by Ódén.*

* *Zeitsch. physikal. Chem.*, 1912, **80**, 709.

Mr. H. M. Ridge suggested that the condition of electric oil emulsions was very important in view of the ore flotation processes now in use, in which enormous masses of material were worked up into oil emulsions. He thought it was only to be expected in such cases that considerable differences of electric potentials would be produced between different parts of the mixture. In the treatment of ore by emulsion methods there was frequently about 1 per cent. of sulphuric acid present.

Mr. Ridsdale Ellis (*communicated reply*): Considering Mr. Hatschek's criticisms with regard to the use of the term "stability," this term was used in a purely relative sense, since, as Mr. Hatschek pointed out, the globules were of such size that the emulsion largely separated out in the course of a few weeks. The fact that the emulsions were never permanently stable was not of importance, as the position of the minimum rate of settling was the essential factor to determine. The emulsions employed were the finest obtainable by shaking the pure oil with pure water, and the use of an emulsifying agent was not feasible, as it would tend to alter the contact potential.

A series of tests on the accuracy of the nephelometer with emulsions of known strengths were made, and it was found that if, as Professor Porter suggested, the concentration of the oil was kept sufficiently low, an accuracy of 10 per cent was obtainable. The more usual concentrations were only one part of oil in 20,000 of water. The effects of gravity made microscopic counts and measurements a matter of considerable difficulty.

The theory of the electrical double layer was a difficult one to crystallize into an exact concrete form. In the first place he believed, and he thought Professor Donnan shared his view, that there were two layers of ions or of charged particles around each globule, an inner negatively charged and an outer positively. Such a globule might not repel another similarly surrounded globule, but would move towards the anode when placed in an electric field owing to a slip or displacement between the two layers (Theory of Helmholtz). The ions forming the outer layer on the side nearest the cathode might move into the body of the solution and their place be taken by ions entering the outer layer on the anode side and flowing over the surface of the globule in the direction of the cathode.

Similarly, with regard to the double layer preventing coalescence in spite of the fact that it exerted no appreciable repulsion as a whole on the other particles, this was probably due to the fact that work has to be done in the disruption of the electrical double layer.

With regard to the action of ferric hydroxide as a positive colloid, Mr. Hatschek's "objection" that the ferric hydroxide was deposited on the surface of the glass as well as on the meniscus was one of the assumptions underlying the theory given. The experiments on the filtering action of gels have no point in this connection, as the whole question was the primary cause of the gel formation and not the action of a gel after it has been formed. Further, the experiments made with aluminium silicate show that the phenomenon is most certainly not a purely mechanical one.

The question of oil flotation processes is a very difficult one, and the present results do not touch them sufficiently to enable anything definite to be said about them.

VOLTAIC CELLS CONTAINING THE SAME SALT DISSOLVED IN TWO DIFFERENT SOLVENTS.

By Principal A. P. LAURIE, M.A., D.Sc.

(*Abstract of a Lecture delivered before the Faraday Society on Tuesday, December* 10, 1912, Dr. T. Martin Lowry *in the Chair.*)

If a salt is shaken up with two different liquids which do not mix, and in both of which the salt is soluble, the salt is shared between the two liquids in a definite proportion.

For dilute solutions this proportion remains the same, and the ratio is known as the partition coefficient.

If after shaking up together the liquids are allowed to separate from each other and two similar electrodes are introduced, there will be no e.m.f. between the electrodes.

The particular case, to take an example, of water, ether, zinc sulphate with zinc electrodes, was investigated by Luther.*

The mathematical investigation of such cells was undertaken by Abel,† and the following is the simplest statement of the condition of equilibrium in such a cell :—

Let P_w and P_s be the solution pressures of the metal in the two solvents w and s, and let c_w and $\bar{c}_s$ be the ionic concentration of the metallic ions in the two solvents after they have been shaken up together.

Then we have—

$$E = RT\left(\log\frac{P_w}{\bar{c}_w} - \log\frac{P_s}{\bar{c}_s}\right) = 0.$$

If some different concentration of the salt be taken, then at the boundary of contact the concentrations will be $\bar{c}_w$ and $\bar{c}_s$ respectively, and therefore each section of the cell can be regarded as an ordinary concentration cell, with the concentration changing from C_w to $\bar{c}_w$, and from C_s to c_s respectively.

If the v_w and u_w and v_s and u_s are the ionic velocities in the two solutions, the expression for the e.m.f. becomes—

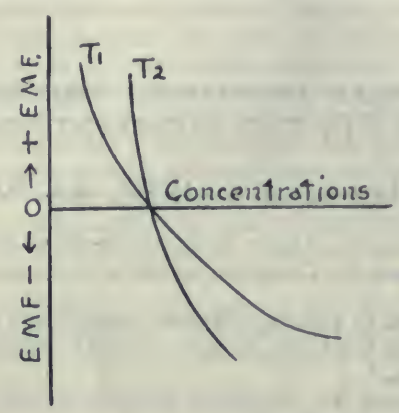
$$E = \frac{2v_w}{u_w + v_w}\frac{RT}{m}.\log.\frac{C_w}{\bar{c}_w} - \frac{2v_s}{u_s + v_s}\frac{RT}{m}.\log\frac{C_s}{\bar{c}_s}.$$

If instead of two liquids which do not mix we select two liquids which do mix, the problem is complicated by their mixing at the boundary, and so

* *Zeit. Phys. Chem.*, xix., p. 567, 1896. † Ibid., lvi., p. 612, 1906.

forming intermediate solvents, and therefore for their proper investigation we must imagine them separated by a third solvent which mixes with neither, but the different solubilities of the salt in each liquid will produce an e.m.f., and enable us to determine therefore the partition ratio electrically.

In order to investigate these cells I used little stoppered vessels inverted and plunged in the solution, and a Dolazelek electrometer. Such stoppers,



if not greased, form a sufficient electrical connection, while preventing mixing.* The cells I used consisted of potassium iodide and iodine, dissolved in water and nitrobenzene with platinum electrodes, potassium iodide and iodine, dissolved in water and ethyl alcohol with platinum electrodes, and potassium iodide in water and ethyl alcohol with silver, silver iodide electrodes.

My first experiments were with the view of testing the effect of temperature on the cells.

If we plot concentration against e.m.f. for two different temperatures in ordinary concentration cells, keeping the concentration the same on one side and changing it on the other, then the curves obtained are as shown above.

The curves cross at zero e.m.f., and with the reversal of the e.m.f. the temperature coefficient is reversed, the cells being always endothermic and the temperature coefficient + -ive.

In the cells under discussion the curves are of the form shown on the opposite page.

With the reversal of the e.m.f. the temperature coefficient is not reversed, the cell becoming exothermic and giving out heat as well as producing an electric current.

If we take the case of potassium iodide in water and alcohol the cell is exothermic when the current is in the direction of transferring potassium iodide from water to alcohol, the ratio of about 1 to 20 being the concentration for no e.m.f.

If a cell is constructed which has no e.m.f. at T_1, then on raising the temperature to T_2 a current flows in the direction to transfer potassium iodide from alcohol to water, and the cell is endothermic.

* *Proc. Roy. Soc. Edin.*, vol. xxxi., part iii., p. 387, 1911.

On now cooling to T_0 the current is reversed and the cell is exothermic, the potassium iodide being re-transferred from water to alcohol, the whole forming a very neat heat engine.

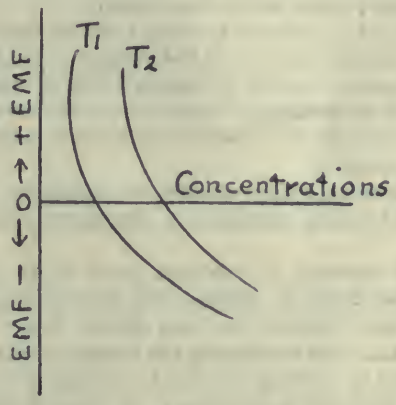
It is evident that if the rate of change of solubility of the salt with temperature was the same in both solutions, then on raising or lowering the temperature no e.m.f. would be produced.

Experiments proving these conditions of e.m.f. with temperature were made with the three types of cell already described.

In iodine, potassium-iodide, alcohol, water cells with ·025 molecule of potassium iodide on each side the equilibrium for iodine is ·0138 molecule in water against ·086 molecule in alcohol.

The next problem is to find the source of energy in these cells which makes it possible for them to be exothermic.

To take the case of potassium iodide in water and alcohol, or any other convenient solvent, it is evident that during the passage of a given current a molecule of potassium iodide is transferred from the one solution to the other. As without the ionic transfer numbers for both solvents we cannot



define what the amount of this current will be, we shall, so as to simplify our equations, define as unit current the amount required to effect this transference of one molecule.

During this transference a molecule of the salt is removed from the one solvent and dissolved in the other. If λ' is the latent heat of solution of 1 gramme molecule of potassium iodide in water (calling heat absorbed + -ive), and λ the latent heat of solution of an equal quantity in alcohol, then when the salt is transferred from alcohol to water—

$$E = \lambda' - \lambda + T\frac{de}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As heat is absorbed when potassium iodide is dissolved, then if λ' is greater than λ, heat is absorbed in the cell during the change, and the cell is endothermic. If, however, the concentrations are so arranged as to transfer the salt from water to alcohol, then the equation becomes—

$$E = \lambda - \lambda' + T\frac{de}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the cell is exothermic.

For equation (1) $T\frac{de}{dT}$ has a + -ive value, the e.m.f. rising with increase of temperature, and for equation (2) $T\frac{de}{dT}$ is — -ive.

Starting from saturated solutions which are necessarily in equilibrium for solvents which do not mix, and applying van't Hoff's equation for latent heats, exactly the same result is arrived at, the change of e.m.f. with change of temperature—

$$de = (\lambda' - \lambda)\frac{T_2 - T_1}{T_1}, \text{ that is } \lambda' - \lambda = T\frac{de}{dT}. \quad . \quad . \quad . \quad . \quad (3)$$

It is evident that if the transfer numbers are also known these equations enable us to measure the differences between the latent heats of solution in very dilute solutions of a salt in two different solvents.

So far we have considered the alcohol as behaving like a solvent that does not mix with water. It remains to be seen how far this view must be modified, and to describe the particular case of water-alcohol-potassium iodide cells with silver, silver iodide electrodes.

The result of the e.m.f. measurements is to show that these cells are in equilibrium when the solutions are in the ratio of 1 molecule of potassium iodide in alcohol to 20 molecules of potassium iodide in water.

Now the solubility of potassium iodide in alcohol is ·096, while in water it is 6·2, so that if the results are correct equilibrium would not exist when both solvents were saturated

Experiments with a saturated solution of potassium iodide in alcohol against saturated and strong solutions of potassium iodide in water confirm this.

When the water solution is saturated there is an e.m.f. transferring potassium iodide from water to alcohol, and the equilibrium e.m.f. is only reached when the water solution has been diluted to the strength of about 2 molecules to 1,000 c.c., thus confirming the former results.

If alcohol is added to a strong solution of potassium iodide in water, the potassium iodide is partially precipitated. It seemed therefore necessary to investigate the limits of this precipitation by adding alcohol in large excess, already saturated with potassium iodide, to water solutions of potassium iodide.

The result of these experiments was to show that the potassium iodide is precipitated until the water content is reduced to 2·1 molecules per 1,000 c.c.; that consequently if a saturated solution of potassium iodide in alcohol is in contact with a 2·1 molecule solution in water no precipitation will take place, but all stronger solutions are precipitated until this dilution is reached. We arrive, therefore, at a modified definition of the partition coefficient between two liquids which inter-diffuse, and of which one is able to partly precipitate salt out of the other.

Two such solutions are in partition equilibrium when the ratio of the strength of solution is such that when the weaker solvent is saturated the stronger solvent is sufficiently diluted to prevent any precipitation of salt by inter-diffusion.

In the case of water, alcohol, and potassium iodide, this ratio is 1 to 20 instead of 1 to 60, the ratio of saturation.

There still remains the interesting question of the source of energy in such a cell when the salt is saturated on both sides and yet the cell is exothermic. I suggest that it is due to the heat set free by the ionic mixing

of water and alcohol, due to the carriage of water and alcohol across the boundaries combined with the respective ions.

Much further investigation, however, would be necessary to test this hypothesis, and, to sum up, I only claim here to have established the relationship between the latent heats of solution and the e.m.f.'s of such cells, and to have shown the condition of equilibrium for mutually diffusing solvents, when one solvent tends to precipitate from solution the salt in the other.

The full details will be found in the paper in the *Proceedings of the Royal Society of Edinburgh* (vol. xxxi., part iii. (No. 24), p. 375) already referred to.

COLLOIDS AND THEIR VISCOSITY.

A GENERAL DISCUSSION.

At the Meeting of the Faraday Society held on Wednesday, March 12, 1913, at the Chemical Society, Burlington House, London, W., a **General Discussion** on **Colloids and their Viscosity** took place. In the absence of the President, **Mr. Emil Hatschek** was in the chair.

The Chairman having accorded a hearty welcome to the guests of the Society who had specially come from abroad to take part in the meeting, Professor Henri, Professor Pauli, Professor Freundlich, and Dr. Ostwald, **Dr. Wolfgang Ostwald** (Leipzig) made an introductory statement on "The Importance of Viscosity for the Study of the Colloidal State."

THE IMPORTANCE OF VISCOSITY FOR THE STUDY OF THE COLLOIDAL STATE.

By WOLFGANG OSTWALD (Leipzig).

I. The subject which the Faraday Society has chosen for discussion at to-day's meeting may at first sight appear an extremely special one. Every investigator who has worked, if only incidentally, at modern colloidal chemistry, knows the extraordinary variety of its phenomena, and the breadth of its laws, relations, and points of view. How does it happen that from this plethora of colloidal problems the Council of the Faraday Society has chosen the special question of the viscosity of colloidal systems and has deemed it a suitable subject for an evening's discussion? It is true, as a well-known physical chemist has said, that one approaches the centre of the earth wherever one may dig into it, that, in other words, the close study of any group of phenomena may lead to the most general laws. Nevertheless we know that there is a difference between different sets of phenomena, inasmuch as some may lead to important general results more rapidly and more directly than others. I may therefore be permitted to choose as the principal subject of my contribution a statement of the reasons for this choice of subject and attempt to explain the significance of the experimental and theoretical study of viscosity for our knowledge of the colloidal state.

II. As the first point of view, which renders the study of the viscosity of colloidal systems so particularly interesting and important, I should mention *the enormous qualitative and quantitative variability* of the viscosity of substances

in the colloidal state. The range of phenomena is in itself extremely diversified and rich. We are accustomed to look on the viscosity of typical molecular dispersoids, such as a sugar or a salt solution, as defined by only two variables if we keep to the same dispersion medium. The viscosity of a molecular solution is in the present state of our knowledge defined completely by the concentration and the temperature. We are considering a system of only three variables, and can therefore plot strict viscosity-concentration curves at constant temperature, and viscosity-temperature curves at constant concentration.

The viscosity of colloids presents an entirely different case. If we take the simpler case of *suspensoid* colloids, *i.e.*, those systems in which the disperse phase still retains the properties of the solid state, at least *one* further variable of the viscosity enters into the matter, the size of the particles or degree of dispersity. It seems as if the maximum of viscosity appeared at medium values of dispersity, the question being for the present left open whether the size of the particles affects the viscosity directly or indirectly, *i.e.*, through the variable quantity of adsorbed dispersion medium associated with it.*

A considerably greater number of variables, however, defines the viscosity of the *emulsoid* colloids, especially of those which become emulsoid through formation of solvates, such as gelatin, albumin sols, etc., also the cellulose and rubber sols, several lubricants, etc. In addition to the three variables : (1) concentration, (2) temperature, and (3) degree of dispersity, the following factors are already known experimentally to affect the viscosity of these systems :—

(4) Solvate formation : the viscosity increases parallel with the amount of dispersion medium taken up by the disperse phase.

(5) Electric charge or ionization. As has been shown for albumin sols, by E. Laqueur and O. Sackur and others, but especially by Wo. Pauli and his pupils, ionized albumin particles, which travel in the electric field, impart to the system a materially larger viscosity than uncharged particles. The influence of the electric charge on the viscosity of hydrated emulsoids is most closely connected with the influence of the degree of hydration ; the two effects run parallel to each other at least in strongly dissociating media like water. I may dispense with a detailed discussion of this point, as the leading authority in this field, Professor Pauli, will personally report on these relations.†

(6) *The Previous Thermal Treatment.*—A gelatin sol which has been repeatedly warmed and cooled has, at least at first, a lower viscosity at the same temperature than a similar sol which has not been thus treated. On prolonged heating chemical changes, such as hydrolysis, frequently occur, which are *no longer reversible*, not even after prolonged standing.

(7) *The Previous Mechanical Treatment.*—A decrease in the viscosity of gelatine sols, and also of several dye-stuff solutions, can be produced by simply forcing the same several times through the viscometer, evidently an indication of a kind of "structure" even in such liquid sols. A special form

* See E. Hatschek, *Koll.-Zeitschr.*, 11, 280, 284 (1912).

† It would be of great interest to ascertain if such a parallelism exists in feebly or non-ionizing media, *e.g.*, in cellulose or rubber organosols. In this case a comparison between the dielectric constants and "dissolving or swelling capacity" on one hand, and between the viscosities of sols of equal concentrations in different media on the other, would be required. The possible influence of the variable charge on suspensoid colloids has likewise not received investigation so far. Theoretically such an influence is to be expected, as the magnetic field induced by the particle must act as a brake on its mobility.

of preliminary mechanical treatment is the mastication of solid colloids, *e.g.*, of rubber *before* dissolving. It is well known that samples of rubber thus treated give *less* viscous sols than untreated samples at the same temperature, concentration, etc.

(8) *Inoculation with Small Quantities of More Viscous Colloids.*—Small additions of viscous colloid after some time raise the viscosity of gelatin or dye-stuff solutions to an incomparably higher degree than would correspond to the increase in concentration due to the addition.

(9) *Time.*—The time factor, finally, is perhaps the most striking variable of the viscosity of hydrated colloids. In all determinations of the viscosity of typical examples of such colloids different values are obtained according to the *age* of the sol, according to the *velocity* with which, *e.g.*, the temperature is altered, etc. Generally speaking the viscosity *increases* with age and tends asymptotically to a final value. The age-viscosity curve appears in the most general case to be S-shaped.* As regards the influence of the rate of temperature change and so forth, much more complicated relations appear to hold good. The alterations of viscosity with time are influenced by additions in the most varied manner.

If we mention in conclusion that (10) *additions* of both electrolytes and non-electrolytes may raise or depress viscosity in the most varied manner, that these effects in their turn depend strongly, both qualitatively and quantitatively, on the concentration of the additions, that with some additions suspensoid colloids also show distinct variations of viscosity with time, that there exist transitional systems with the most varied intermediate steps as regards viscosity, we certainly obtain the picture of an enormous *qualitative* diversity in the phenomena of viscosity in colloids. We are thus dealing with a group of phenomena large and interesting in itself.

The same thing, however, also holds good of the *quantitative* variations of the viscosity of colloidal systems. I would ask you to remember that a gelatin sol may, merely by altering temperature or concentration, or even by mere ageing, pass through all values of viscosity from that of water to that of a solid, as occurs in a process of gelatinizing. For the viscosity of a colophony-turpentine sol, according to measurements by Glaser, the values between concentrations of 0 to 100 per cent. range from 1 to 10^{∞}. It is particularly remarkable, that such enormous changes of viscosity can occur even within *extremely small* ranges of temperature or concentration. Thus an agar sol between 0 and 1 per cent. concentration passes through all values of viscosity from 1 to several thousand. What is more, soap sols and certain complex organic compounds † can attain the viscosities of solids at concentrations lower than 1 per cent. Change of temperature has a similar marked effect, as shows itself, for instance, practically by the existence of "melting-points" and "setting-points." Thus the viscosity of colloidal solutions is distinguished by extreme variations as regards quantitative relations too.

III. In addition to the importance of viscosity phenomena as forming an extremely varied field for investigation, a further weighty consequence follows from the great variability just set forth: the determination of viscosity is a prominent *methodic principle* in investigating the properties of the colloidal state, but especially in the study of those processes in colloidal systems which are usually described as *changes of state.* If it is desired to follow quantitatively the alterations of dispersity and of solvate formation,

* See Wo. Ostwald, *Grundr. d. Kolloidchemie*, 3 ed., 1912, p. 191.

† See, for instance, the papers by E. Hatschek, *Koll.-Zeitschr.*, **11**, 158 (1912); W. B. Hardy, *Proc. Royal Soc.*, A, **87**, 29 (1912); B. Rassow and O. Doehle, *Koll.-Zeitschr.*, **12**, February, 1913.

which are called peptization, coagulation, gelatinization, imbibition, etc., in principle any physicochemical property of the system may be used as indicator of such changes. Practically, however, very considerable differences manifest themselves again between the various selected properties. Thus, for instance, the electric conductivity of a gelatine sol does not change materially during setting. Neither does ultra-microscopic observation permit us at present to follow this process quantitatively. The reason is that such properties either *do not vary sufficiently* during a given change of state, or that they are *not suitable for quantitative investigation.* That property of a colloid will, generally speaking, be best suited as an indicator which shows

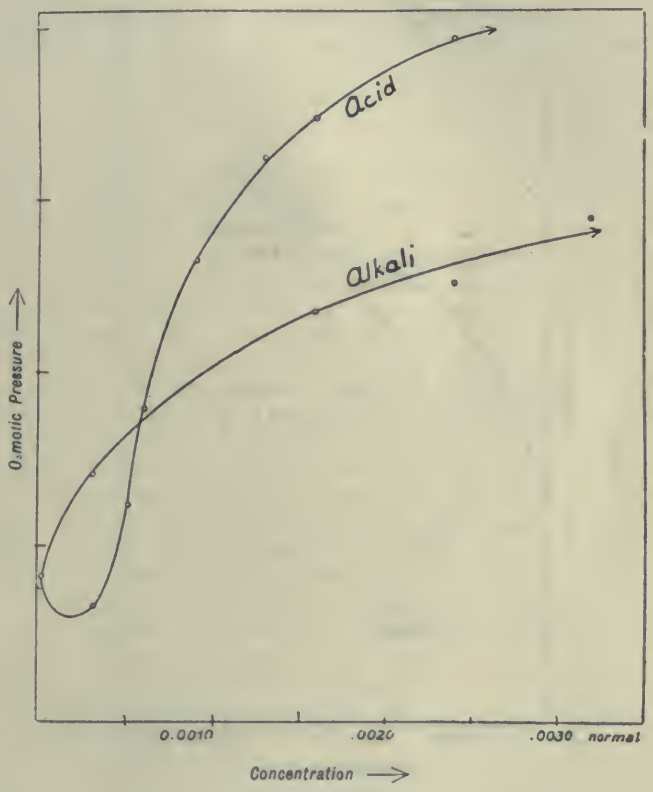


FIG. 1.

the largest possible variation with small changes in the colloidal condition, and on the other hand permits quantitative measurements, if possible by a method not too complicated. These requirements are eminently fulfilled by the viscosity. The extreme sensitiveness of this constant towards very small alterations in the condition of the colloid has already been described. On the other hand, you are, of course, aware that viscosity determinations, especially with the capillary viscometer, are not too difficult.

The question now arises, in what way can viscosity measurements give information even on such changes as, *e.g.*, gelatinization and swelling by imbibition, changes in which to some extent the properties of *solids* are

involved. Closer investigation gives the important result, that in these processes the *concentration of the colloid*, while certainly playing some part quantitatively, does *not* essentially affect the qualitative character of the phenomena, which the viscosity of *dilute* colloids shows under the same experimental conditions. Thus Wilh. Ostwald and J. von Schroeder have first shown that spontaneous increase with time in the viscosity of dilute gelatin sols corresponds entirely with the setting of more concentrated sols. With increasing concentration the viscosity of the sols increases in increasing but entirely *continuous* ratio, until at certain concentrations or times it attains the values of a jelly, that is of a solid. The curves at different concentrations are throughout of the same character ; additions also affect the viscosity of

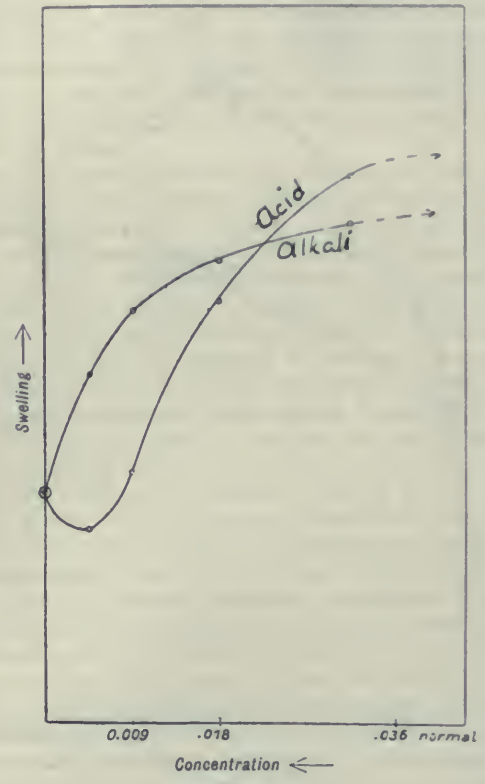


FIG. 2.

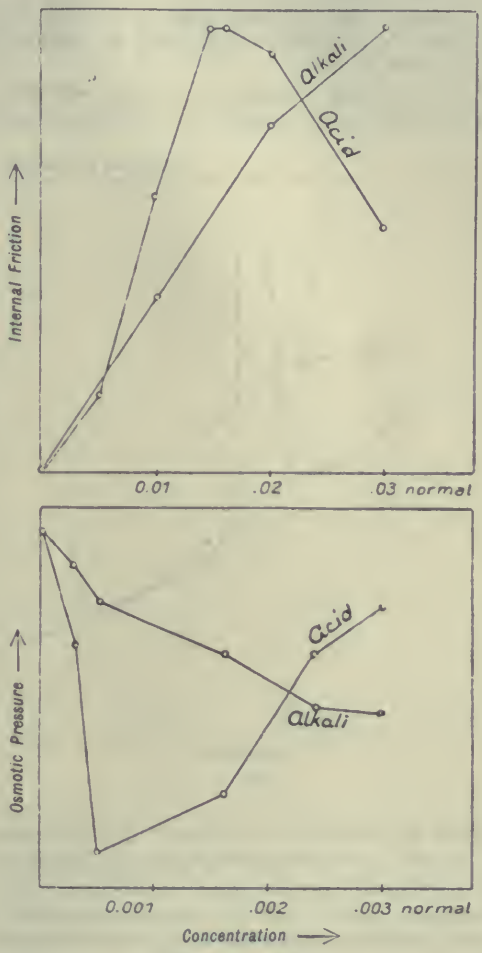
dilute sols and the setting of concentrated sols qualitatively in exactly similar ways.

Entirely analogous considerations apply to the study of swelling and imbibition phenomena. Although not much studied from this point of view, even liquid sols show such imbibition phenomena.* Such are the absorption of water by gelatin and albumin sols, also by some dyes, which have been observed in osmometers and have been called "osmotic" or perhaps more correctly "pseudo-osmotic."† Without entering into details, we may

* Wo. Ostwald, *Grundr. d. Kolloidchemie*, 3 ed., p. 312 sq.

† The expression "pseudo-osmotic" is preferable, as these phenomena deviate in many ways quite considerably from the classical osmotic phenomena of molecular systems.

emphasize that the pseudo-osmotic imbibition of a gelatin sol corresponds most strikingly, on one hand with the swelling phenomena in the *solid* colloid, and on the other with the viscosity changes of the same colloid in suitable experimental conditions. The following figures may elucidate this point. Fig. 1 represents the effect of acid and alkali on the pseudo-osmotic pressure, determined experimentally, of a 1·5 per cent. gelatin sol according to R. S. Lillie. Fig. 2 shows the influence of the same additions on the swelling of gelatin according to experiments by Wo. Ostwald. The



FIGS. 3 AND 4.

agreement of the curves down to details is striking. On the other hand, Figs. 3 and 4 illustrate the connection between pseudo-osmotic pressure and viscosity of albumin sols on addition of acid and alkali, the former from experiments by R. S. Lillie, the latter after Wo. Pauli and his pupils. The curves again agree, but are reversed : an *increase* of viscosity corresponds to a *decrease* in pseudo-osmotic pressure, etc. The agreement between the phenomena of viscosity, gelatinization, swelling, and pseudo-osmosis of such colloids is astonishingly complete down to details. The absolute acid con-

centration at which the first *minimum* of swelling occurs for gelatine is the same as coincides with the corresponding *maximum* of viscosity; similarly the pseudo-osmotic pressure of sols varies, like the viscosity, with shaking, stirring, the thermal history, etc. In brief, we are dealing with a complex of phenomena most intimately connected with one another, which permits us to draw from one property far-reaching conclusions as to the behaviour of other properties.* Among all these properties at present viscosity occupies *a central position*, as it is so far the most accessible and the most easily measured property.

Two further instances may perhaps be given showing the application of viscosity measurements to problems which have so far received little or no treatment from this point of view.

Fig. 5 shows the viscosity changes of a dilute *albumin sol on heating*. The temperatures are plotted as abscissæ and the logarithms of the times as

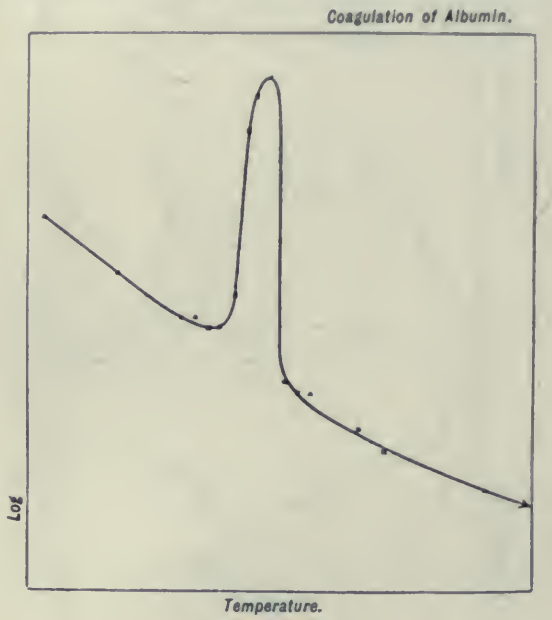


FIG. 5.

ordinates. Between 50° and 57° the viscosity at first decreases in an entirely normal manner. At 57·5°, however, shortly before the appearance of turbidity, a large increase of viscosity occurs, which at about 60° gives place to an equally steep decrease. After that the viscosity curve of the coagulated suspensoid albumin continues practically in the same direction, as if nothing had happened.

Another interesting example is the viscometric behaviour of a *starch suspension during heating*, a process which leads to the well-known *gelatinization* ("kleisterbildung"). This is shown in Fig. 6, the ordinates being the same as in the preceding figure. Here also the decrease in the viscosity of the suspension is at first entirely normal—possibly the extreme regularity deserves mention (the curve is a straight line). An astonishingly sharp change or break

* The author pointed out the parallelism between viscosity and swelling eight years ago. (*Pflüger's Arch.* 108, 563 (1905), 109, 277 (1905), 111, 581 (1906).)

then occurs between 57° and 58·5°,* which leads to an equally remarkable steep increase, also in a straight line. Between about 65° and 75° the curve has a sharp bend and then continues, from 80° on, to rise exceedingly steeply. The curve shown here only continues to 95°; it is, however, known that at still higher temperatures, say at 110° and 120°, the starch is transformed still further into its so-called *soluble* form. This is distinguished by *no longer gelatinizing, i.e.*, a solution treated at 120° is *less* viscous again than the same solution at about 90°. At still higher temperatures a *drop* in viscosity may therefore be anticipated, such as has been indicated by the arrow.

In yet another respect viscosity determinations appear to possess special importance as a methodic principle. The existing methods for measuring

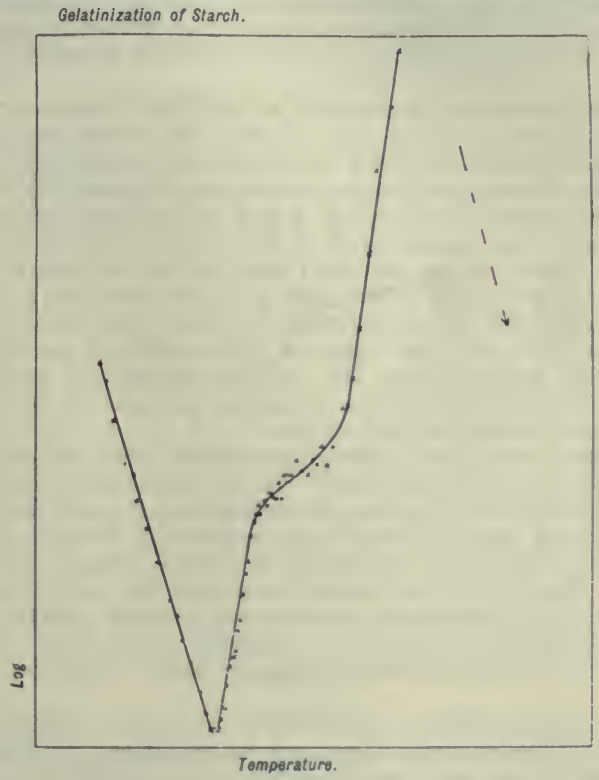


FIG. 6.

changes of state depend, with extremely few exceptions, on the determination of *points*. Peptization, coagulation, setting and softening *points* have been determined, *i.e.*, definite concentrations or temperatures, at which the process in question reaches a "perceptible" or "pronounced" value. The imperfection of this method is shown by experience; thus, for instance, coagulation points, *i.e.*, temperatures, and concentrations differing among one another by 30 to 40 per cent. have sometimes been obtained. Of course, this does not amount to saying that such determinations of points may not occasionally lead to valuable results, but the method is not, in any case, an ideal one. The

* This temperature of gelatinization agrees entirely with that found by optical methods by M. Samec (*Koll. Beihefte*, 3, 129 (1911)).

author has ere this tried to emphasize* that these *static* methods for determining changes of state must be replaced by *kinetic* methods. The ideal case of a strict definition, *e.g.*, of a coagulation, consists in establishing the *velocity equation* of the process, and then in characterizing the effects of various coagulations and their concentrations by the numerical values of the *velocity constants*. It is only in quite recent times that such *kinetic* investigations and measurements have been applied to changes of colloidal state. We may refer to the work of H. Chick and C. J. Martin on the heat coagulation of albumin sols, H. Paine's investigations on the velocity of coagulation of colloidal copper, etc. Viscosity is again to a high degree suitable as indicator property for such kinetic investigations, the more so as it does vary not only during the changes of hydrated emulsoids, but also during the coagulation of metal sols, as has been shown by H. W. Woudstra † among others. Without doubt we have here still a large and fertile field for the application of viscosity measurements.‡

IV. The author may be permitted to point out a third field, in which viscosity measurements promise to be of great value for the knowledge of the disperse state. As you are aware, modern colloidal chemistry has led to the fundamental conclusion that *continuous* transitions are possible between coarse suspensions, colloidal solutions, and systems of molecular dispersity. The first convincing experimental proof of this fact was furnished by H. Picton and S. E. Linder (as long as twenty years ago, in Sir William Ramsay's laboratory) with their well-known series of arsenic trisulphide sols. It was, however, only modern colloidal chemistry which drew the above conclusions from these and other important experiments and pointed out the advantage of studying rather the common features, and especially the *transitional phenomena*, instead of attempting unsuccessfully to draw sharp demarcations between the three classes.§

Nowadays, indeed, these transition phenomena occupy the first place in the attention of the colloidal chemist. He determines the dependence of all possible properties and processes on the degree of dispersity, and finds the most interesting transitions towards the behaviour of molecular dispersoids of analogous composition ; the work of The Svedberg may be quoted as an instance. Viscosity has been studied remarkably little in this connection. A number of such transitional systems on the border of colloidal and molecular dispersity may, however, be mentioned, which show pronounced *anomalies of viscosity*, peculiarities which in many ways recall those of colloids.

Such systems are, first of all, the *critical mixtures of liquids, e.g.*, butyric acid-water at certain temperatures and concentrations. J. Friedländer,‖ V. Rothmund¶ and others have shown that an *enormous rise* of viscosity takes place in such mixtures on cooling *before* the separation into a macroheterogeneous system. While, for instance, at a certain temperature, the viscosities of water and isobutyric acid are 1·12 and 1·48 respectively, the viscosity of their critical mixture at the same (or indeed a slightly higher) temperature amounts to 3·68. The anomaly becomes even more marked if

* Wo. Ostwald, *Grundr. d. Kolloidchemie*, 1 ed., 1909, p. 267.

† H. W. Woudstra, *Koll.-Zeitschr.*, 8, 73 (1911), where references to earlier work are given.

‡ I see that Professor Freundlich is going to demonstrate at the meeting an interesting case of such a kinetic investigation, corresponding exactly to the suggestions quoted above.

§ *Koll.-Zeitschr.*, 1, 298, etc. (1907).

‖ J. Friedländer, *Zeitschr. phys. Chemie*, 38, 404 (1901).

¶ V. Rothmund, ibid., 63, 54 (1908).

the *temperature coefficients* are considered, *i.e.*, the percentage increase in viscosity per degree (or the logarithms of the times of transpiration). Thus the percentage increase in the viscosity of a critical water-isobutyric acid mixture with 38·6 per cent. of acid at 0·15 from the point of saturation amounts to *34·3 per cent. per degree.* This enormous increase obviously recalls the behaviour of gelatinizing colloids. If we bear in mind that both the gelatinizing of colloids and the increased viscosity of critical mixtures are accompanied by increased opalescence, etc., the analogies often referred to between critical separation and gelatinization become still more marked.

Other systems with entirely analogous anomalies of viscosity are, for instance, *liquid sulphur* above 130° and the opalescent fused *crystalline liquids.* Here, too, we meet with enormous temperature coefficients of viscosity, accompanied by optical and other phenomena which vividly recall

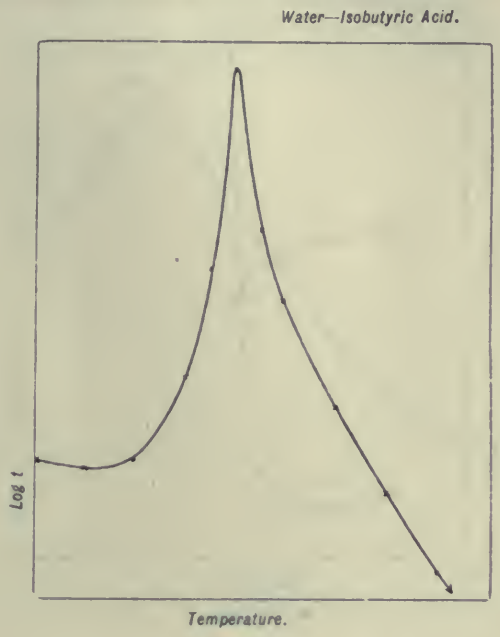


FIG. 7.

analogies with colloids. On cooling molten sulphur from about 400° to about 200° the viscosity rises from 150 to about 50,000, to fall again to 8 at about 150°.* The viscosity of molten sulphur also depends on the previous thermal treatment, and the general temperature-viscosity curves are, as regards shape, almost identical for critical mixtures, crystalline liquids, and fused sulphur, as Figs. 7–9 show.†

* L. Rotinjanz, *Zeitschr. phys. Chemie*, **62**, 609 (1908).

† Curve 7 after V. Rothmund, *loc. cit.*; 8 after E. Bose and F. Conrat, *Physikal. Zeitschr.*, **9**, 169 (1908); 9 after L. Rotinjanz, *loc. cit.*

The analogy between the viscosity of molten sulphur and of critical mixtures was first emphasized by the author in his *Gundriss der Kolloidchemie*, 2nd edition, p. 130, note. H. R. Kruyt (*Z. phys. Chemie*, **81**, 726 [1913]), has recently objected to this comparison between the curves of L. Rotinjanz and J. Friedländer as showing "not much" similarity, since the coordinates of these curves do not correspond; he accordingly declines to admit the analogy. The author admits that indeed Friedländer's curves are not immediately suitable for this comparison, although even these show the qualitative agreement between the anomalies of viscosity. The

A certain similarity with the curves of albumin coagulation and of the gelatinization of starch can also be hardly overlooked.

It is hard to believe that this extremely far-reaching agreement of the curves should be only external. On the contrary, general colloidal chemistry here appears to be called upon to settle finally controversies of long standing, such as the question : are crystalline liquids or critical mixtures *homogeneous* or *heterogeneous*?* This same question, as you know, has for years been the central point in the discussion of *colloidal* systems. Modern colloidal chemistry here replies, that normal colloids, critical mixtures, crystalline liquids, molten sulphur, etc., are all *disperse* systems, *i.e.*, systems whose properties are periodically discontinuous is space, this period being extra-

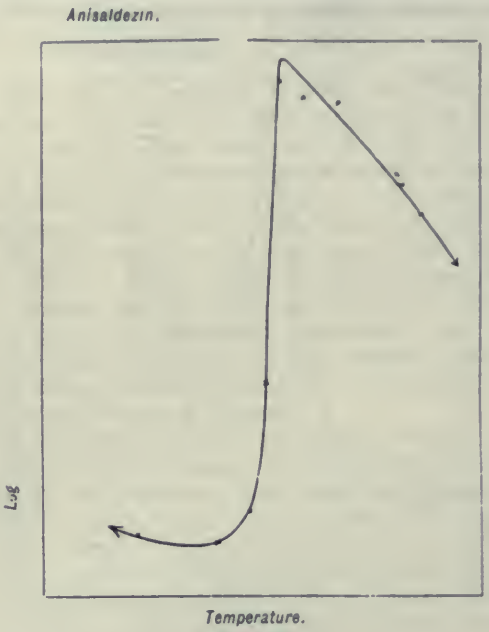


FIG. 8.

ordinarily small. This of course applies equally to molecular systems and to coarsely heterogeneous ones, and the definition is thus much more general than any definition based on the theory of phases. The more special questions arise only in the second place, such as the questions of the degree of dispersity, the solid or liquid state, the formation of solvates, etc., of the disperse portion, in brief, the kind and number of properties which still show periodical discontinuities in the system under consideration. It is purely a matter of definition which discontinuities are to be considered as characteristic for a *system of several phases*, if a disperse system is to be described as such, and thus the contrast homogeneous–heterogeneous has no longer any justification in fact for such systems. This dispute has, indeed, one may say

curves after V. Rothmund, however, which the author of course knew when writing the above note, show the agreement asserted by him in the most desirable manner, as will be seen from Figs. 7 and 9. Perhaps these figures will have a more convincing effect on H. R. Kruyt.

* See Wo. Ostwald, *Koll. Beih.*, 4, 1 (1912); as regards crystalline liquids also *Koll.-Zeitschr.*, 8, 269 (1911).

almost imperceptibly, disappeared from the discussion. The agreement here demonstrated between the anomalies of viscosity in systems *apparently* totally different from one another surely justifies us in considering such systems together experimentally from the point of view of the theory of disperse systems.

V. In conclusion, I should ask to be permitted to make a few remarks on the importance of viscosity measurements in the field of *applied* colloidal chemistry, and in regard to both scientific and practical applications. Of the former must be mentioned the viscosimetric examination of *blood* and of the body fluids generally, both in the normal and the pathological state. A literature of several hundred papers, devoted to this one application of the viscosity of colloids, is already in existence.* Nor is there any doubt that many further investigations in this field are required, to ascertain which of

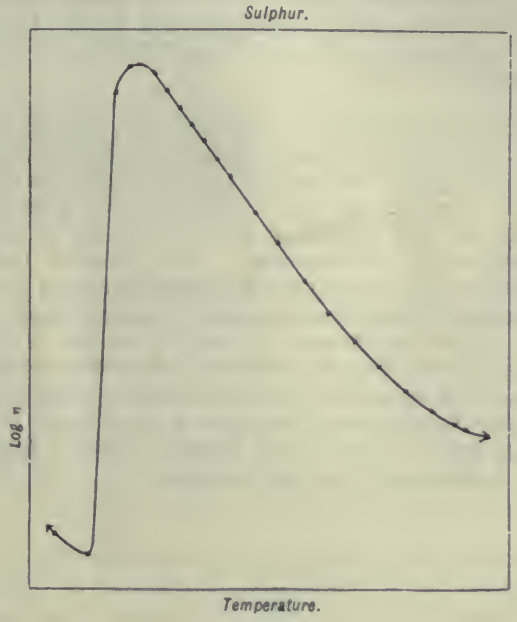


FIG. 9.

the very numerous variations observed so far may be used, *e.g.*, for diagnostic purposes. It is not surprising that the results obtained so far in these researches appear somewhat complicated. Even the exact viscometric study of simpler colloids is in many ways still at the first stage of its work, that of elucidating phenomena, so that even here it is rarely possible to speak of quantitative comparisons.

A particularly interesting *technical application* of viscosity determinations we find in the chemistry of indiarubber. A large number of investigators (S. Axelrod, P. Schidrowitz, C. Beadle and H. P. Stevens, H. Fol, and others, see particularly the last issues of the *Koll.-Zeitschrift*) have pointed out that the viscosity of rubber sols may give a clue to the physical properties of the undissolved rubber. Thus, in general, the "nerve" of rubber

* See, for instance, the list by G. Rossi in 1906 (*Arch. di. Fisiol.*, 3, 507), which already contains 127 references.

corresponds to a higher viscosity of its solution ; "killed," *i.e.*, depolymerized rubber which has been rendered less elastic, gives lower viscosities at the same concentrations than rubber not thus treated mechanically, etc. It has sometimes been stated that the viscosities of rubber sols depend on so many factors that their practical application appears impossible. The problem may have a large, but certainly not a practically infinite, number of variables, and a systematic study may take much time, but is certainly neither impossible nor as uninteresting or unimportant as it may perhaps appear to some rubber experts. It must of course be admitted that such a practically exhaustive and systematic investigation of the viscosity of even an ordinary aqueous emulsoid has never yet been carried out. Such a monographic investigation of some selected colloid would certainly be of the highest value as a standard example of the technical application of viscometry.

Many further applications besides those quoted may be mentioned. Such are the *analytical* use of viscosity measurements in estimating the value of glue, starch, and adhesives, the viscometric examination of oil, lubricants, and similar complex systems, etc.

I think I cannot conclude my remarks on the importance of viscosity measurements for the study of viscosity better than by pointing out that the official founder of colloidal chemistry, Thomas Graham, has himself drawn attention to this point. As you know, this many-sided investigator was one of the first authors who carried out any viscosity—or, as they were then called, "transpiration"—measurements. It is therefore intelligible that Graham should have noticed the peculiar variability of just this property in colloidal systems, and should have emphasized its importance. In this sense he said "*that a liquid transpiration tube may be employed as a colloidoscope.*" This surely expresses an unusual appreciation of the importance of viscosity measurements, on the part of the founder of colloidal chemistry.

I hope I may be expressing the views of the Council of the Faraday Society if I propose that we regard Graham's words, "*The viscometer as colloidoscope,*" as the motto of to-day's meeting.

THE DETERMINATION OF THE SIZE OF COLLOIDAL PARTICLES.

Professor Victor Henri (Paris) read a Paper on "The Determination of the Size of Colloidal Particles."

The determination of the viscosity of colloidal solutions is of very great importance, as it is possible to arrive at a knowledge of the structure of a given colloidal system by measuring this physical constant.

One of the first questions which presents itself is the relation between the size of the colloidal particles and the viscosity. The well-known researches of Einstein, of Hatschek, and of many other authors have shown that in the case of a colloidal system formed by spherical particles suspended in a liquid the viscosity is given by the formula—

$$\eta' = \eta \left(1 + K\frac{v'}{v}\right)$$

where η' is the viscosity of the colloidal solution, η that of the continuous phase, v' the total volume of colloidal particles, v the total volume of the system, and K a constant equal, according to Hatschek, to $\frac{9}{2}$. According to this theory the viscosity of a colloidal solution should be independent of the size of the particles, and this is indeed the result which Bancelin has obtained experimentally with suspensions of gamboge and of mastic. Experiments by Sven Oden on colloidal sulphur have, however, not confirmed this theoretical result, as the viscosity increases when the size of the particles decreases.

Where the particles are deformable or have no fixed dimensions, and can alter their volume by imbibition, the problem becomes extremely difficult.

It will, therefore, be apparent that the first thing necessary is to be able to measure the size of the particles. We shall review the different methods which can be employed, and point out the sensitiveness of each method in different cases.

1. *The Method of Direct Measurement by the Ultra-microscope.*—This is the method used from the beginning by Siedentopff and Zsigmondy. It consists in making a count of the particles contained in a definite volume, and in determining the weight of substance dispersed in this volume. This method is applicable in a limited number of cases only. One has to assume that the composition of the particles is the same as that of the dry substance, and also that the whole of the substance is represented by the particles visible in the ultra-microscope, and that consequently there are no amicrons and no true solution.

Very frequently, however, the composition of the particles differs greatly from that of the residue obtained by precipitation or evaporation, as, for instance, in the case of ferric hydrate, the ferrocyanides, the sulphides, etc. Even in very simple cases, *e.g.*, the colloidal metals prepared by Bredig's

method, a portion of the substance, sometimes very considerable, is dissolved in the continuous phase as oxide. Thus M. Rebiere has found, in the laboratory of the Sorbonne, that sols of Ag prepared with very pure distilled water contained up to 30 per cent. of silver in a state of solution.

To apply this method correctly it is therefore indispensable to separate the continuous phase by filtration through a collodion filter, and to analyse the dry residue and the filtrate separately.

2. *The Method of Measuring the Density of Distribution at Different Heights.*—This method is founded on the classical work of Perrin. In applying to a suspension which has attained a state of equilibrium the law of the equal distribution of energy, Perrin has shown that the following relation holds good :—

$$2{,}303\ W \log \frac{n_0}{n} = 2\pi r^3(\rho - \rho')gh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where—

W is the mean molecular energy $= \frac{3}{2}\frac{RT}{N}$.

N Avogadro's number $= 7 \cdot 10^{23}$.

n_0 and n the numbers of particles found in equal volumes at the levels o and h.

g the gravity constant.

ρ the density of the solvent and ρ' that of the particles.

r the radius of the particles.

By substituting for W its value at ordinary temperature (T = 290) in C.G.S. units we obtain—

$$\log \frac{n_0}{n} = (\rho - \rho') \frac{h \cdot r^3 \cdot 10^{17}}{1 \cdot 9} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If accordingly we count with the ultra-microscope the numbers n_0 and n of particles at two levels, the vertical distance of which is h, and if we know the densities ρ and ρ', we can easily calculate the radius r of the particles.

The table below gives for instance the diameters of particles of gold, silver, and oil, which correspond to a ratio of $n_0 : n = 10$ for heights h equal respectively to 1 mm., 0·1 mm., and 0·01 mm.

	Au. $\rho' = 13{\cdot}27$.	Ag. $\rho' = 10{\cdot}5$.	Oil. $\rho_1 = 0{\cdot}9$.
$h = 1$ mm. ...	44$\mu\mu$	54$\mu\mu$	248$\mu\mu$
$h = 0{\cdot}1$ mm. ...	94$\mu\mu$	118$\mu\mu$	534$\mu\mu$
$h = 0{\cdot}01$ mm. ...	202$\mu\mu$	252$\mu\mu$	1,148$\mu\mu$

To carry out the measurements, the microscope is arranged horizontally and the solution placed in a small cell with parallel faces, from 0·1 to 1 mm. deep, according to circumstances. As ultra-microscope the Zeiss paraboloid or the Reichert or Leitz condensers may be used. An objective with very great frontal distance should be used. The eyepiece is provided with a square ruled micrometer, the distance of the lines being gauged exactly. By shifting the preparation vertically through known distances it is easy to make counts of the particles at different levels.

This method has the advantage of being very exact. For the same ratio $n : n$ the height h varies very rapidly with the size of the particles.

With this method it is necessary to know the density of the particles. In the case of metallic sols large differences in the density affect the value of the radius but little, so that in these cases an uncertainty as to the density amounting to as much as 50 per cent. has little influence on the calculated value of the radius.

3. *The Method of Measurement of the Brownian Movement.*—Einstein (1906) has shown that the mean square of the displacements along a straight line undergone by a particle in the time t is—

$$L^2 = 6\delta t$$

where δ is the diffusion constant.

The mean square of the projections l on an axis of displacement is—

$$l^2 = 2\delta t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By applying to colloids the formulas of Stokes and of van't Hoff, Einstein has obtained the following relation between the diffusion constant, the size of particles, and the viscosity of the medium—

$$\delta = \frac{RT}{N} \frac{1}{6\pi r\eta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which the symbols mean—

R the gas constant $8{,}32 \cdot 10^7$ (C.G.S.).
N Avogadro's number, $7 \cdot 10^{23}$.
r the radius of the particles.
η the coefficient of viscosity of the medium.

From (3) and (4) follows the relation—

$$r = \frac{RT}{N} \cdot \frac{t}{3\pi\eta l^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For colloidal solutions in water at ordinary temperature we have the values $\eta = 0{\cdot}010$ (C.G.S.), $T = 293$, and accordingly—

$$r = 3{\cdot}7 \cdot 10^{-13} \frac{t}{l^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus, for instance—

For $r = 100\mu\mu$ and $t = 4$ secs. $l^2 = 14{\cdot}8 \cdot 10^{-8}$ cm., and $l = 3{\cdot}8\mu$.
For $r = 10\mu\mu$ „ $t = 4$ secs. $l^2 = 148 \cdot 10^{-8}$ cm., „ $l = 12\mu$.
For $r = 1\mu\mu$ „ $t = 4$ secs. $l^2 = 1{,}480 \cdot 10^{-8}$ cm., „ $l = 38{\cdot}5\mu$.

It will be seen that the higher the degree of dispersity the better applicable is this method.

In carrying out the measurements it is necessary to take into account a whole series of sources of error which may vitiate the results. A layer of sufficient thickness to eliminate the effects of the walls must be observed; at least fifty observations should be made for each grain and the amount of displacement in one direction ascertained every 4 seconds, for which purpose a carefully gauged square ruled grating in the eyepiece is employed.

The accuracy of this method is rather low, as the radius varies with the square of the displacement. Very exact measurements have been carried out by Chaudesaignes.*

* *C.R. Acad. d. Sc.*, 1911.

4. *Determination of Size of Particles by Measuring the Speed of Settlement.*—Stokes's formula applied to colloidal solutions permits us to determine the size of the particles, if the viscosity and density of the medium and the density of the particles are known. The formula is—

$$v = \frac{F}{6\pi\eta r},$$

where v is the speed and F the force applied to the particles, which is—

$$F = \frac{4}{3}\pi r^3(\rho - \rho')g.$$

By substituting this value for F we obtain—

$$r^2 = \frac{9}{2}\frac{\eta}{(\rho - \rho')g}v \quad \ldots\ldots\ldots\ldots \quad (7)$$

If we take colloidal gold in water we have at 20 $\rho - \rho' = 18{\cdot}27$, $\eta = 0{\cdot}010$, $g = 980$ cm., and thus—

$$r^2 = 2{\cdot}51 \,.\, 10^{-6}r.$$

If accordingly we measure the time taken in sinking 0·1 mm. we get—

For $r = 1{,}000\mu\mu$	the time for 0·1 mm.	is	2·5 secs.
For $r = 100\mu\mu$	„	„	250 secs.
For $r = 10\mu\mu$	„	„	25,000 secs. = 7 hrs.

It will be seen that the method can be applied only to coarse suspensions, at about the limit of microscopic visibility.

5. *Determination of the Size of Particles by Diffusion.*—Sutherland (1905), Einstein (1905), and Smoluchowski (1906), have established the following relation between the diffusion constant δ, the viscosity, and the radius of the particles—

$$\delta = \frac{RT}{N}\frac{1}{6\pi\eta r} \quad \ldots\ldots\ldots\ldots \quad (8)$$

Sutherland, Cunningham,* and Milliken† have extended this formula to cases to which Stokes's formula does not apply, when it takes the following form—

$$\delta = \frac{RT}{N}\cdot\frac{1 + A\frac{a}{r}}{6\pi\eta r} \quad \ldots\ldots\ldots\ldots \quad (9)$$

where A is a constant of the approximate value 0·815 and a is the mean path of the molecules of the solvent. The correction term disappears when the radius of the particles is large compared with the mean path.

If we consider colloidal solutions in water at ordinary temperature, the formula becomes—

$$\delta = 1{,}83{\cdot}10^{-13}\frac{1}{r}\ (\text{cm.}^2\ \text{sec.}) = 1{,}58{\cdot}10^{-8}\frac{1}{r}\ (\text{cm.}^2\ 24\ \text{hr.}).$$

Thus, for example—

For $r = 1\mu\mu$	...	$\delta = 18{,}3{\cdot}10^{-7}$ cm.² sec.	= 0·158 cm. 24 hr.
For $r = 10\mu\mu$	...	$\delta = 1{,}83{\cdot}10^{-7}$	„	= 9·9158	„
For $r = 100\mu\mu$	...	$\delta = 0{,}183{\cdot}10$	„	= 0·00158	„

* *Proc. Roy. Soc.*, 1910.
† *Phys. Zeitschr.*, 1910.

If we bear in mind that the diffusion constant for urea is 0·97 (cm.² 24 hr.), we see that the diffusion method can be used only in the case of very highly disperse systems, such as have been studied by Herzog, Svedberg, and Dabrowski.* The best procedure is certainly that of Dabrowski; but in any event, this method is very slow, as it requires experiments extending over weeks or even months, and is applicable only to sols which do not alter with time. These considerations compel one to treat with some scepticism the results obtained on albumin, which is stated to contain particles of 2·9 to 1·43$\mu\mu$.

6. *Determination of Sizes of Particles by Absorption of Light.*—The experiments and theoretical studies of Garnett,† of Mie,‡ of Wood,§ of Svedberg,‖ have shown that there exists a close relation between the size of particles and the absorption of light by colloids.

Our knowledge of the optical properties of colloids is not yet sufficiently advanced to allow us to deduce for any given sol the size of the particles from the coefficient of absorption. We can, however, for any one solution, follow the change in size by studying the variation of the adsorption, as has been done by Svedberg.

It seems that frequently the absorption coefficient is proportional to the volume of the particles, *i.e.*, equals $\frac{r^3}{C}$; the method therefore shows small variations in the size.

For practical purposes it is advisable to determine the absorption coefficient for small wave-lengths, and especially for the ultra-violet. As an instance we may quote an investigation on a silver sol prepared by Bredig's method in very pure water; the sol contained per litre 0·14 gr. of silver in the colloidal and 0·020 gr. in the dissolved state, as oxides. Measurements of the absorption coefficient ε, carried out by the method of spectro-photometry with a quartz spectrograph, and calculated by the formula—

$$f = f_0 . 10^{-\varepsilon d},$$

where d is the thickness in cm., gave the following values of the coefficient ε—

$\lambda = 600\mu\mu$	500	450	360	355	344	340	333	325	**321**	318	310	305
$\varepsilon = 1·4$	1·7	2·5	2·5	2·3	1·7	1·15	1·0	0·54	0·51	0·55	0·78	1·0

300	290	275	260	250	236	226	220
1·15	1·52	1·70	1·90	2·0	2·2	2·5	2·7

The curve below represents the absorption spectrum of colloidal silver. It will be seen that there is a very pronounced *minimum* of adsorption m, which corresponds to $l = 321\mu\mu$. This is exactly the same value of l at which Hagen and Rubens have found the maximum for the transparence of metallic silver in very thin films.

For equal silver contents we have found that the position of the minimum of absorption varies little, but on the other hand the degree of adsorption for $\lambda = 321$ varies a good deal with the size of particles. One may therefore hope to find in this method a means of determining the size of particles by means of the absorption coefficient.

7. *Determination of the Size of Particles by Measuring the Intensity of Light Diffused Laterally.*—Lord Rayleigh (1871) has shown that the intensity of the

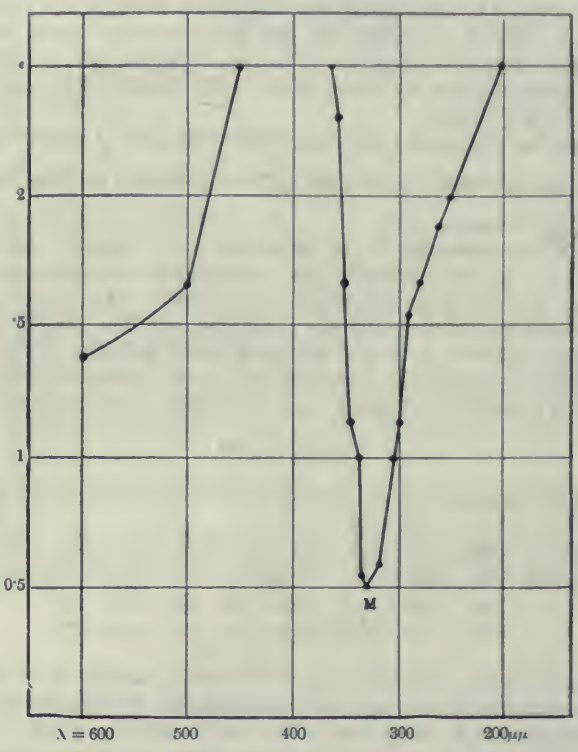
* Acad. of Cracow, 1912.
† *Phil. Trans.*, 1904, 1905.
‡ *Ann. d. Phys.*, 1908.
§ *Physical Optics.*
‖ *Existenz d. Moleküle*, 1912.

light diffused laterally by a suspension through which a beam of light of known intensity is projected is given by the following expression—

$$i = \frac{A n r^6}{\lambda^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where A is a factor dependent on the refractive indices of the medium and the particles, the intensity of the incident beam, and the angle at which the diffused light is observed, n is the number of particles and λ the wave-length of the diffused light.

If the number of particles remains constant, the intensity of the light diffused laterally grows as the sixth power of the radius; it accordingly varies extremely rapidly, which is the reason why Tyndall's method is so



sensitive in revealing the smallest traces of colloids, even if they are very highly dispersed.

The formula (10) shows that the intensity i grows very rapidly as the wave-length λ decreases.

This method is very sensitive and gives exact results even in the case of very fine suspensions. Practically it is convenient to work with violet or ultra-violet light, which is projected through the liquid placed in a quartz cell with four parallel faces. The cell is placed against the slit of a spectrograph, and the spectrum of the light diffused at right angles to the incident beam is photographed. Given the exposures, it is easy to determine photometrically from the spectrograms the intensity of the diffused light for each value of λ. Experiments which I have made will be published elsewhere.

The subjoined table gives a summary of the methods for determining the sizes of colloidal particles.

Method.	Quantities to be Determined.	Relation between Quantities Determined and Radius.	Limit of Applicability.
Variation of concentration with height	ρ, ρ^1	$hr^3 = K \log \frac{n_0}{n}$	$r > 50\mu\mu$
Brownian movement ...	η	$l^2 r = Kt$	$r < 50\mu\mu$
Velocity of settling ...	η, ρ, ρ^1	$r^2 = Kv$	$r > 100\mu\mu$
Velocity of diffusion ...	η	$\delta r = K$	$r < 10\mu\mu$
Light absorption	—	$r^3 = K\varepsilon$	—
Lateral diffusion of light	—	$r^6 = Ki\lambda^4$	—

It will be seen that, according to the size of the particles, one or the other of these different methods has to be applied. If a certain degree of accuracy is to be attained it will, however, be necessary to employ several methods simultaneously.

THE VISCOSITY AND ELECTROCHEMISTRY OF PROTEIN SOLUTIONS.

Professor Wolfgang Pauli (Vienna) read a Paper on "The Viscosity and Electrochemistry of Protein Solutions."

The proteins may be said to be foremost among those colloids to which viscosimetry has been applied in a comprehensive and varied manner, and if I have to-day the honour of presenting a report on this extensive domain to your Society, I shall have to impose upon myself a certain, perhaps even a one-sided restriction.

Proteins, as every investigator has had to learn to his sorrow, are characterized by a bewildering variety of physical changes of state, as well as by a far-reaching reactivity with electrolytes and colloids. Almost all these relations betray themselves by simultaneous changes in the viscosity, which frequently enable us to make a quantitative estimate of the change in the solutions of the proteins. We may put it as a general rule for the variations in the viscosity of protein solutions, that the changes are caused by variations, not of the properties of the dispersing medium, but of the properties of the dispersed particles, be they fluctuations in their solubility or their associations, sometimes possibly alterations of the surfaces of the protein particles connected with adsorption effects. Most frequently, however, changes in the hydration, or to use Freundlich's term, in the lyophily, will be the basis of the increase or decrease in the viscosity. Most frequently again the causes of the variations in the hydration will be found in changes of the electric charges. Thus arises the intimate connection between the electrochemical properties and the viscosity of protein solutions, which is to be the chief subject for my consideration to-day. That we have a rich selection of examples at our disposal, we owe largely to British investigators such as Hardy and Bayliss, whose names are coupled with the fundamental inquiries into the physical chemistry of albumins, and Ramsden, Moore and Roaf, Chick and Martin, and others, who subsequently published important contributions to the investigation in this so promising field.

To render the subject more lucid I will divide my material into two main sections: The behaviour of albumin within the isoelectric range, and its behaviour without that range.

I.

All proteins, which predominantly consist of mono-amino acids, are amphoteric electrolytes in which the acid character prevails; their acid-dissociation constant k_a is therefore greater than the basic-dissociation constant k_b. For this reason the proteins contain, in their pure solutions, next to the neutral particles M, chiefly anions and H-ions, and only a very small number

of kations and of OH-ions. In an electric field such an albumin, as I, Bottazzi, and Michaelis have demonstrated, will show a distinct migration towards the positive pole. When we gradually add acid to the solution, the H-dissociation of the protein will be impeded. At a certain concentration of the H-ions the number of the albumin-anions will be equal to that of the kations. At this point the solution will not display any uni-directional migration with the electric current. A further addition of acid will rapidly increase the positive albumin-ions, while the acid will be bound. Following Hardy and Michaelis, we call this critical point in the electric behaviour of the albumin its iso-electric point.

This isoelectric point is characterized by a certain concentration of the H-ions and by other features. The number of the positive albumin-ions is not only equal to that of the negative albumin-ions, but the former number is, as L. Michaelis deduced, a minimum, and that of the neutral particles is a maximum. According to Michaelis we hence characterize the isoelectric point by the relation—

$$A = \frac{k_a \cdot M}{(H^{\cdot})} \text{ and } K = \frac{k_b \cdot M}{(OH')},$$

where M designates the number of neutral particles, A that of the anions, and K that of the kations.

When K = A, we have for the isoelectric point—

$$\frac{k_a}{k_b} = \frac{(H^{\cdot})}{(OH')}.$$

Thus the H-ion concentration at which the isoelectric state is reached would apparently be independent of the protein concentration. In making this deduction we have tacitly assumed, however, that the structure of the albumin-ions has remained unchanged by the addition of acid to the solution until the isoelectric point is reached. That presumption is not always justified, however. Yet we may practically disregard this objection and consider the relation as valid, provided certain regulators be applied for the reaction, *e.g.*, an acetic-acid and acetate mixture for arriving at the desired H·-concentration. This has extensively been done by Michaelis. By means of transference experiments he found for the isoelectric reaction in—

Serum albumin ... ... $2 . 10^{-5}$ H·,

and likewise in—

Glutin... ... ... $2 . 10^{-5}$ H·.

We have been able to confirm these results working under the same experimental conditions.

The question arises now whether other properties of the proteins mark a reversal at the isoelectric point which, we have seen, designates also a maximum number of neutral particles and a minimum of albumin-ions. This is really the case. Thus R. Chiari has found in our Institute that the swelling of glutin has a minimum at this point. Sörensen and Jürgensen observed, with high albumin percentage, an optimum H·-concentration for the denaturation by heat, which seemed to correspond to this point. On the strength of experiments conducted in conjunction with J. Matula, I may add that the coagulation produced by alcohol has its optimum at this point.

Not only does the isoelectric concentration, as determined by the aid of the precipitation with alcohol, agree with the electrophoretically determined value for albumin and glutin, but the coagulation by alcohol is probably, wherever applicable, the most simple and elegant method, and by virtue of the fine gradation of which it admits by varying the protein and alcohol proportions, the most suitable method for determining the isoelectric point. It also enables us to demonstrate the independency of the isoelectric concentration from the protein percentage.

The common feature now of all the last-mentioned methods of swelling coagulation by heat and precipitation by alcohol is the fact that the isoelectric point shows a maximum of dehydration. The idea therefore suggested itself to investigate changes in the isoelectric state also by means of viscosimetry, and a decrease in friction was to be anticipated. This decrease I was indeed able to establish, by proceeding with certain precautions, together with Matula. The minimum of viscosity exactly occurs at the isoelectric point. The following table summarises the observations on the internal friction in purest dialysed ox-serum and in glutin at different H·-concentrations. The minimum, it will be seen, coincides sharply with the optimum of the coagulation by alcohol.

TABLE.

Viscosity of Albumin + Acetic-acid-acetate Mixture.

H·-ions.	Serum (1 per cent) 25° C. η.	Glutin (1 per cent) 35° C. η.
$0{\cdot}13 \cdot 10^{-3}$	1·0531	1·5796
$0{\cdot}86 \cdot 10^{-4}$	1·0455	1·5509
$0{\cdot}42 \cdot 10^{-4}$	1·0398	1·4977
$0{\cdot}21 \cdot 10^{-4}$	1·0379	1·4769
$0{\cdot}11 \cdot 10^{-4}$	1·0303	1·4885
$0{\cdot}53 \cdot 10^{-5}$	1·0341	1·4954
$0{\cdot}21 \cdot 10^{-5}$	1·0360	—
$0{\cdot}10 \cdot 10^{-5}$	1·0379	—

The rather subtile frictional phenomena are best demonstrated with glutin, and the following diagram (Fig. 1) shows a fine friction curve of glutin, near the isoelectric point; the abscissæ are not the H·-concentrations, but the powers of this concentration, as Sörensen first proposed.

All the experiments so far made concerning the viscosity and other changes of state of proteins in the isoelectric condition are in accord as to concurrence of a maximum of electrically neutral particles with a maximum of dehydration. The subjoined examples may make this relation still clearer ; these examples date from earlier days, and they have guided us in finding new methods for determining the isoelectric point.

II.

As soon as we pass beyond the isoelectric point by further addition of acid, the albumin begins to react decidedly as base and rapidly to bind the acid. Before we consider the viscosity-phenomena under these circumstances, we will attempt to gain an insight into the electrochemical conditions in such acid-albumin-solutions. We will again take the example of hydrochloric acid and serum-albumin in the first instance.

This case—electrometrically first studied by Bugarsky and Liebermann—has recently been re-examined very carefully by K. Manabe (Tokio) and

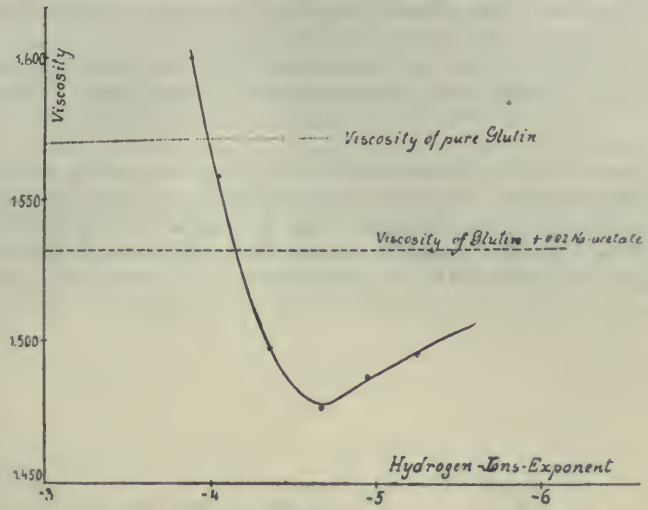


FIG. 1.

Matula in our Institute. They determined at the same time by the aid of suitable galvanic couples the hydrogen- and chlorine-ions in a very precise manner. Diagram Fig. 2 shows the distribution of the hydrogen- and chlorine-ions in a 1 per cent. albumin solution with increasing acid additions

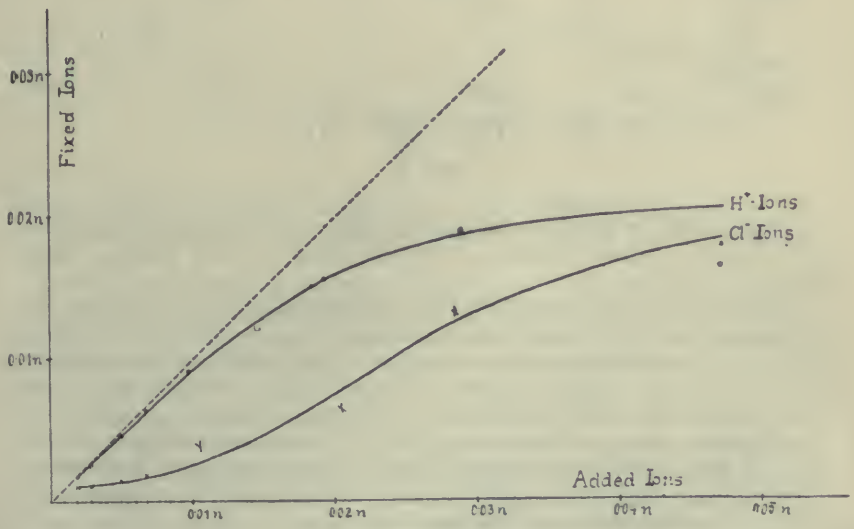


FIG. 2.

beyond the isoelectric point. The experiment demonstrates that nearly all the hydrogen-ions are fixed up to a certain acid concentration, but that a

noteworthy fixation of the chlorine-ions only sets in beyond this concentration, as soon as there is an excess of free hydrochloric acid.

There is no doubt that the excessive acid exerts its influence by suppressing the ionization of the albumin chloride. If we plot a differential curve (Fig. 4) of the fixed hydrogen- and chlorine-ions, this curve passes through a maximum which also represents a maximum of the ionization of the albumin. Beyond this maximum point there is very little further fixation of hydrogen-ions, the maximum of which finally coincides with that of the fixation of the chlorine-ions.

The viscosimetrical examination of acid-albumin now brings out a stupendous increase in the friction up to a maximum, which is followed by a decrease when the acid becomes excessive. Fig. 3 exemplifies this condition for hydrochloric acid and monochloroacetic acid. We may in this instance assume that the increase of friction corresponds to the ionization, the decrease

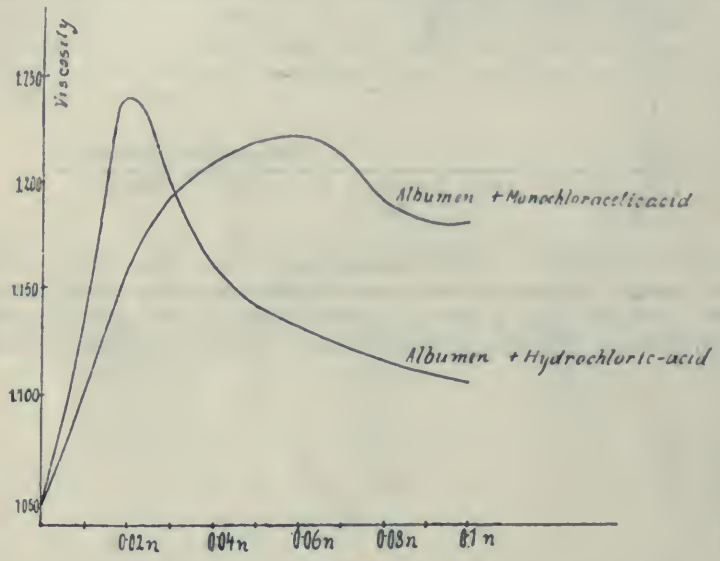


FIG. 3.

to a suppression of the dissociation. The electrometrically found maximum of ionization indeed coincides with the peak of the friction curve (Fig. 4).

The electrometrical investigation of acid-albumin proves that the acid, up to the maximum of its being fixed, is chiefly taken up for the formation of a salt which is capable of ionization, and it must be pointed out that, contrary to other views, it is only the positive ions which contain the albumin, a fact which follows also from the migration in an electric field. In view of the considerable amount of fixed acid and of the high molecular weights of proteins, as well as of the circumstance that a decomposition of the albumin does not occur under these conditions, the single particle of albumin must unite with a large number of acid molecules.

The increase in the friction would therefore be connected with the formation of multivalent albumin-ions. Careful measurements of the osmotic pressure, which I have made in conjunction with M. Samec, point in the same direction. You will see from the following diagrams, in which the ordinates

indicate water-pressures in cm., and the abscissæ the concentrations of the acid, with which the osmotic cell was brought in equilibrium, that the osmotic pressure is raised to a multiple when the addition of acid is continued, finally to fall off similarly as the friction curve, when an excess of acid is present (Fig. 5). Since both the albumin-ions and the corresponding chlorine-ions, which are electrostatically bound, must participate in determining the osmotic pressure, the osmotic pressure curve will also yield a measure for the ionization of the albumin.

If the albumin solution were not associated in its neutral state—a point not definitely decided so far—the increase in the osmotic pressure might enable us to determine the number of chlorine-ions per albumin-ion and thus the valency of the albumin-ion. At present we can only estimate the valency at an optimum figure ranging from 4 to 6. Viscosity measurements of the contents of the osmotic cell, on the other hand, allow us safely to assert that the pressure and viscosity maxima indeed coincide, as we were led to assume.

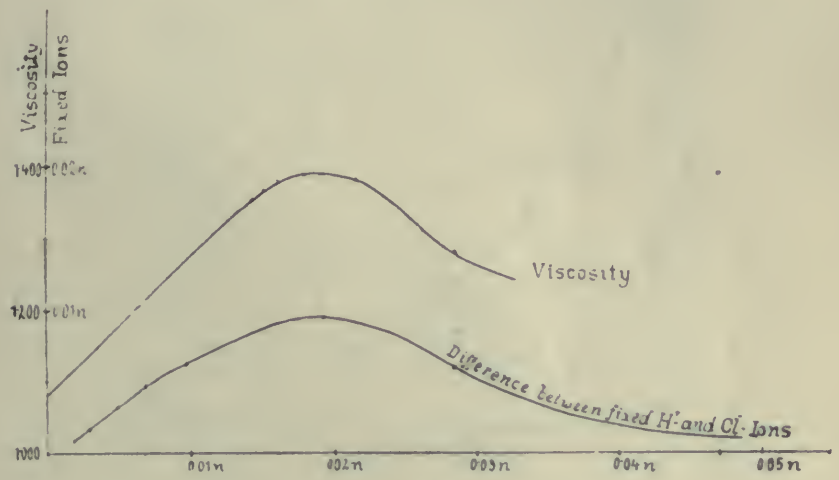


FIG. 4.

Diagram Fig. 6, in which the abscissæ are the concentrations within the cell as deduced from direct chlorine determinations, are instructive in this respect.

If then the experience gained justifies us in ascribing the very large increase in the friction of acid-albumin to the formation of protein-ions possessing several valencies, a further question at once arises as to the cause of this effect of polyvalent protein-ions. The most obvious explanation would be that these ions are characterized by a strong hydration.

The conception of a powerful solvation by the ions need not especially be created for our case. It has been accepted in many quarters in order to account for the relatively small differences in the mobilities of several ions as well as for the transport of water which is connected with their transference by the electric current. Abegg and Bodländer in particular have shown that an increase in the density of the electric charge with increasing valency at decreasing "Haftintensität" promotes the hydration. For this reason we may presume a very considerable hydration of the particles, especially for polyvalent protein-ions.

Chick and Martin have recently attempted to calculate the number of fixed water molecules for the casein-ions in accordance with the theoretical deductions of E. Hatschek. There remain enough difficulties to be explained, however. There is, in the first instance, a decided discrepancy between the friction, as mechanically measured, and the resistance to motion, electrically determined; according to all experience the mobility of the protein-ions is relatively large and in the most unfavourable case not too far removed from Bredig's limit of $18 \cdot 10^{-5}$. Robertson has first directed serious attention to the divergence between the high friction values and the mobility of the albumin-ions, which must exclusively be regarded as the carriers of the high viscosity. For the dispersing medium retains even in highly viscous albumin jellies an almost unimpaired permeability for the various ions. In order to account for the discrepancy between the mobility

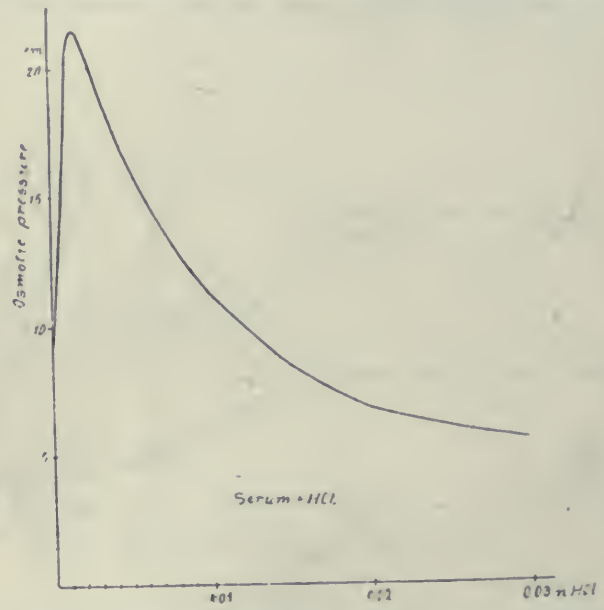


FIG. 5.

in the electric field and the mechanically measured mobility, Robertson has recourse to the hypothesis of a kind of reticular structure of the solutions. Such a reticular grouping of the ions might, in another shape, resuscitate the idea, which had been abandoned for good reasons, that work had to be done in the electric field to effect the separation of the particles as well as their transport. But all the experimental evidence, especially with reference to colloids and proteins, suggests that the associating processes, which build up the structure, concern not the ionized, but the neutral particles. Just in those stages which precede and which follow the increase in friction, and at which we meet with the optimum concentrations in neutral protein particles, we likewise find formation of aggregates and coagulation and, in the case of jellies the maximum tendency to solidification. The suggestion of a structural union of the ions of albumin in the sense of Robertson is not supported by observational evidence, therefore.

With regard to the question of the mobility of the ions and internal friction we must not overlook that there is, according to G. Bredig and H. Euler, a simple antagonism between these values for elementary, mono- or di-valent ions, but that it is more than doubtful whether these relations may proportionately be applied to the complex protein-ion of high valency. In the case of the proteins the internal friction might increase at a more rapid rate than the mobility of the ions decreases. The basis of the comparison between fluidity and mobility of the ions is not sufficiently secure as regards albumin, moreover. In conducting viscosity measurements the difference between neutral and highly hydrated ionized protein has so far been regarded as being independent of the number of electric charges carried by the ions. On the other hand comparisons between viscosity and velocity of the ions have been referred to equivalent mobilities of the ions, whilst in the case of the albumin salts we have no reliable evidence for the normality of the solutions. Yet we may still

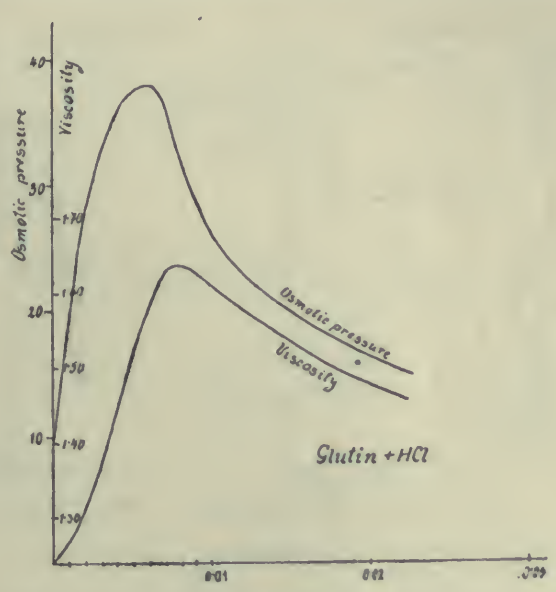


FIG. 6.

expect that the relations between the mobility of the ions and internal friction of albumin solutions will find a satisfactory explanation in the course of time without necessitating any special assumptions.

We have so far confined ourselves to the phenomena of acid-albumins. *Mutatis mutandis*, however, the same arguments may be applied to alkali-albumins. In the latter, the polyvalent negative albumin-ions are the carriers of large friction. In other respects the relations between maximum friction and fixation of base are of a similar character. The phenomena are more difficult to follow up experimentally, however, owing to the greater chemical instability of the negative albumin-ions.

On account of their comparability to their electrolytic solutions, and of the accessibility of their entire isoelectric ranges, albumin and glutin offer important advantages over globulin, which Hardy studied in his fundamental research, and over casein, which has been investigated by Laqueur and

Sackur, Robertson, and others. So far as the comparability goes, there are no differences in principle as to the behaviour of all these proteins with respect to acids and alkaline lyes; the conception of a connection between ionization and hydration has proved fertile throughout these researches.

It is not only acids and alkalis, however, that can cause the formation of polyvalent albumin-ions. Several of the salts of the heavy metals yield with albumin complex salts, in which the albumin, owing to the introduction of several ions of the heavy metals, gives compounds with polyvalent, positive ions which contain the protein. Again we observe a maximum of viscosity, which falls off once more in the presence of an excess of metallic salt. To this maximum of friction corresponds an optimum of electric transference and of electric conductivity, and a minimum of coagulability by alcohol. In the acid-albumin noticeable quantities of free hydrogen-ions were only

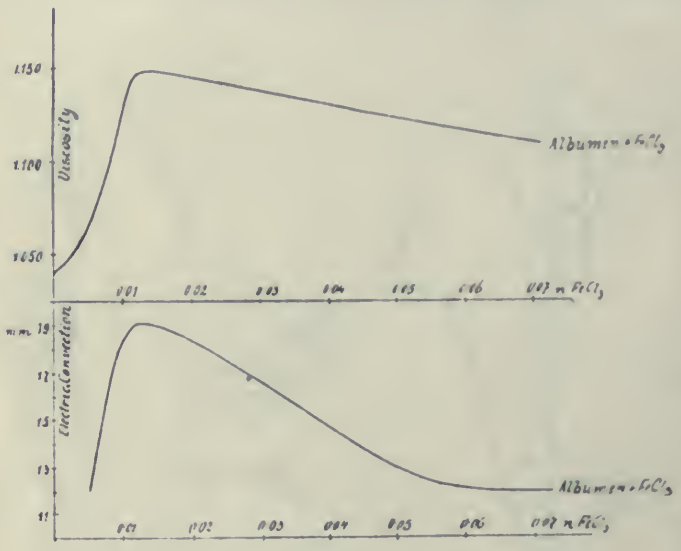


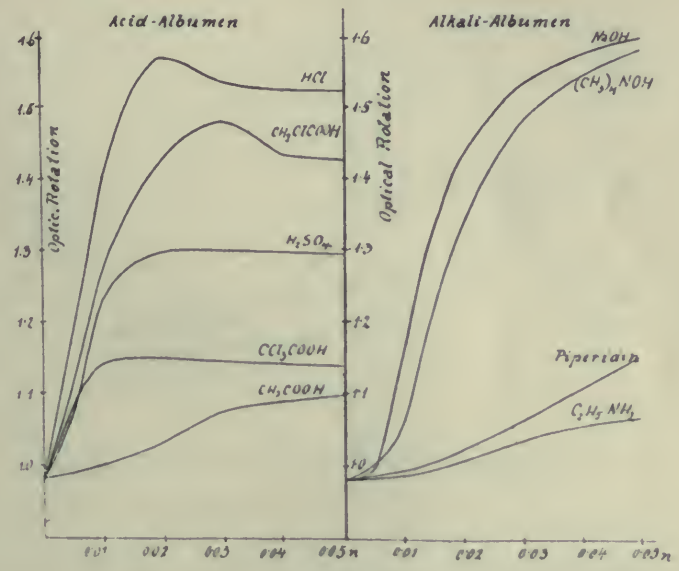
FIG. 7.

observed when the maximum of the viscosity had been exceeded; this again holds for the iron-albumin compound and the ferri-ions.

The following data have been taken from a research which Flecker and I have conducted on the compounds of albumin with heavy metals. You notice in the diagram (Fig. 7), how the viscosity rises, attains its maximum, and diminishes again when more and more ferrichloride is added to the albumin. Next to this curve you see the parallel curve of the transference in the electric field; the increase and decrease in the ionization of the ferri-albumin chloride can directly be read off, and the maximum coincides with the viscosity maximum.

Direct determinations of the fixed hydrogen-ions, as well as measurements of the osmotic pressures, teach us that, under the mild influences of small quantities of acid and of low temperatures, relatively few points of the large albumin-molecule come into question as regards the entrance of hydrogen. What we know concerning the structure of the albumins seems to indicate that it is not only the extreme amino-groups which come into play in this fixation. The following observation of mine points to the same conclusion.

The very large increase of the friction by the addition of acids and alkaline lyes is allied with a certain intactness of the albumin-molecule. That intactness is found to be weaker already in the albumoses, and it has disappeared in the peptones. It is true that we can recognize the transition from the neutral to the ionized state by an increase in the hydration (demonstrated viscosimetrically) in substances down to the simple amino-acids. But the order of magnitude of this change is very different from that holding for albumin. To demonstrate the change, an extremely small increase in the friction, we need an approximately semi-normal solution, whilst the phenomenon is very pronounced with albumin at a concentration of the order 10^{-4} N. already. We understand from this fact also, that the determination of the diminution of the friction constitutes a very delicate and lucid method for tracing the decay of albumin in its very first stages, and that this method is hardly equalled in delicacy by any other method.



FIGS. 8, 9.

We do not really know to-day even whether the formation of the polyvalent ionized albumin—as suggested by the increased viscosity—proceeds simultaneously with structural rearrangements in the albumin-molecule. For the possibility of a structural change speaks, in addition to the strikingly small hydrolytic dissociation of the protein salts, the fact that, as Samec and I have ascertained, the increase in friction runs parallel to an increase in the optical rotation, likewise up to the maximum of friction. But suppression of the ionization by an excess of acid or of alkali very little affects the decrease in the optical rotation, in contradistinction from the effect on the friction ; the importance of the electric charge is therefore decidedly inferior to that of the albumin-salt formation. Diagrams Figs. 8 and 9 reproduce the marked changes in the optical rotation produced in acid- and alkali-albumin.

Similar relations may be shown to hold for the albumin compounds with the heavy metals. Again we observe increase both in friction and rotary power with increased ionization, but constancy of the rotation when the

ionization is impeded by an excess of heavy-metal salt. Yet that changes in friction and in rotary power need not necessarily proceed on parallel lines is shown by experiments with glutin, for which a very large increase in friction (by the addition of acid or alkali) is accompanied by an insignificant increase in the rotary power.

The action of neutral salts on the highly viscous, ionized, and hydrated acid- or alkali-albumin is of very great interest, though the details of the reactions still stand very much in need of elucidation. The striking effects of additions of neutral salts are diminution of friction, restoration of the coagulability by heat and by alcohol, and finally irreversible coagulation. The electric investigation of these cases suggests loss of electric charge by the albumin and hence concomitant phenomena of dehydration and aggregation. Fig. 10 illustrates the decrease in the friction caused by the addition of salt to an acid-albumin. The viscosity measurement is exceedingly sensitive;

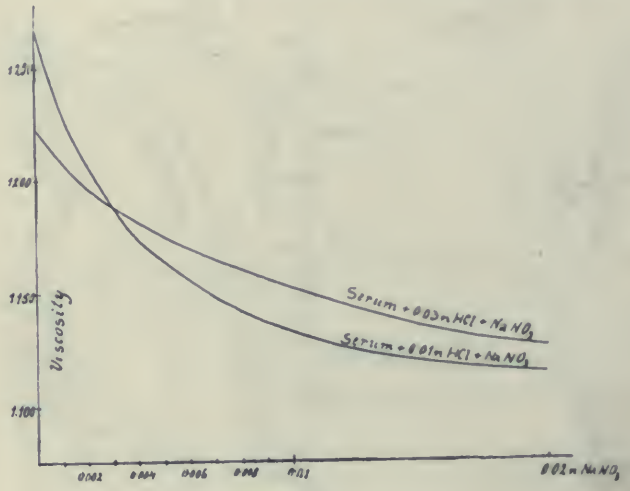


FIG. 10.

with suitable arrangement an addition of N/10,000 salt is sufficient to mark an appreciable diminution.

As to this depression of the viscosity, the various salts may be grouped in a characteristic series of their anions, which series is not quite in accord with the order of the so-called lyotropic effects of the salts. The sequence of the anions with respect to the friction of acid glutin at a constant salt concentration of 0·01 N. is illustrated in Fig. 11. In increasing order of their viscosity depressions the anions are: acetate, fluoride, chloride, bromide, chlorate, nitrate, iodide, rhodanide, trichloroacetate sulphate.

The differences in the ionic series are not the only differences as to the action of salts on ionized and on neutral albumin. In the latter case the well-known series of lyotropic effects begins with the sulphate and ends with the rhodanide. A high salt concentration of from 3 to 5 N. is required to produce coagulation, which is reversible moreover, whilst with acid-albumin a salt concentration of 0·2 N. suffices to produce coagulation, which is not reversible by dilution. In neutral albumin salts, salts give rise to a diminution of the viscosity simultaneously with a reduction of the coagulability, in the acid-albumin to an increase in the coagulability by heat and by alcohol. These

differences suggest also a difference in the mechanism of the viscosity change which is produced by the addition of salts.

Viscosimetry has first revealed an exceedingly interesting case of albumin reaction, viz., the action of certain methylized xanthines on acid-albumin. When coffeïne or theophylline is added to acid-albumin, the viscosity is considerably increased. The effect, and especially that of coffeïne, is very well brought out in the curves of diagram Fig. 12.

When we examine this phenomenon more closely, we recognize that complex salts, *e.g.*, albumin-coffeïne chloride, are apparently formed, which are characterized by a greater hydration than the albumin-chloride itself. So far, however, this peculiarity has only been established for albumin ; it is missing in glutin and fibrin and in the direct decomposition products of albumin.

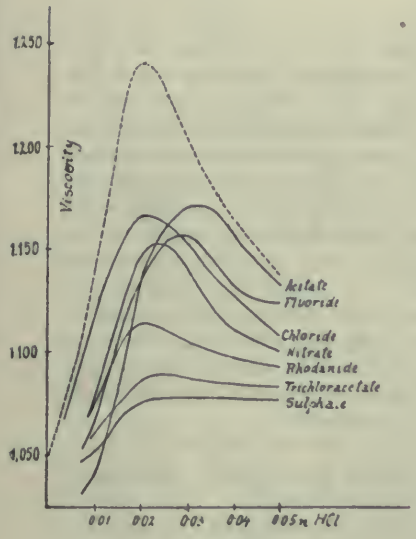


FIG. 11.

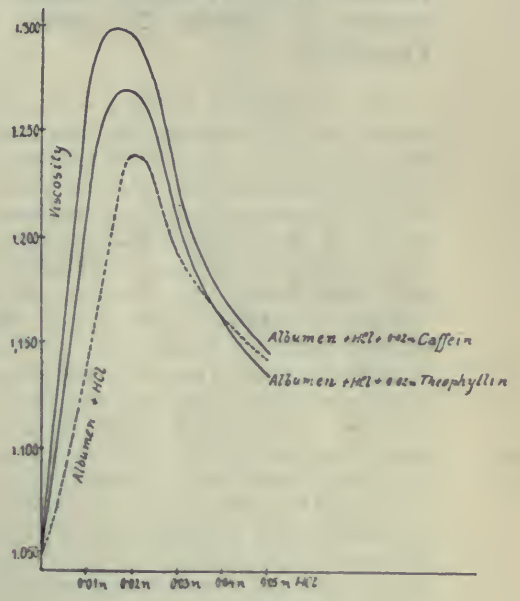


FIG. 12.

Time does not permit me to quote further examples, and I must content myself with pointing out that the importance of viscosimetrical measurements for the observation of structural changes is, as experiments made in our Institute prove, shown also by lecithin emulsions and by starch, which is distinguished by a particular variability and instability of its solutions. I have not touched upon some important issues, such as the relations of concentration and temperature with respect to the viscosity of emulsoids, because these problems form part of the general characteristics of emulsoids, which require a special discussion. But the examples I have selected will certainly show, I think, how very important the determination of the internal friction is just in the case of proteins for the recognition of changes of those unstable substances which we cannot chemically conceive in any other way, and how difficult, and yet promising, the problems are which still remain to be elucidated.

THE RATE OF COAGULATION OF $Al(OH)_3$-SOLS AS MEASURED BY THE VISCOSITY CHANGE.

A Paper "On the Rate of Coagulation of $Al(OH)_3$ Sols as measured by the Viscosity Change," by **Professor H. Freundlich** and **Professor C. Ishizaka** (Brunswick), was presented by Professor Freundlich.

The investigation which I wish to bring before you to-day does not directly aim at elucidating the varied and complicated relations which the viscosity problems of colloidal solutions offer. The original object was to compare the precipitation of $Al(OH)_3$-sols by various anions with the adsorption of these anions by Al_2O_3. It was found, however, that the precipitation of the sol by electrolytes is best studied by the change in the viscosity, as Kawamura* had already done, and that the rate of coagulation can likewise be determined in this way. To-day I should therefore like to report on the results of our measurement of the velocity of the coagulation, without dwelling upon our comparative investigation of colloid precipitation and adsorption—which, it may be remarked, once more demonstrates a decided dependence upon the valency and the readiness with which the anions are adsorbed. Our results exemplify the applicability of the viscosity determinations to problems of the chemistry of the colloids. Indirectly we also learn something concerning the viscosity of the sols themselves.

The $Al(OH)_3$-sols of which we availed ourselves for our experiments were prepared by the method of Crum,† by gradual hydrolysis of aluminium acetate and expulsion of the acetic acid by continued heating. The colloidal solutions look, as is well-known, perfectly colourless, almost like pure water, and are only slightly turbid. Their viscosity scarcely differs from that of water, and the velocity of efflux of the sol in an Ostwald viscosimeter was, *e.g.*, 52 seconds, whilst the value for water was 49 seconds. This hydro-sol is very stable, as Crum already observed; we did not notice any change in the properties after several months, except that the precipitation value had decreased by a few per cent.

When we add to the sol a solution of an electrolyte sufficiently concentrated to effect precipitation, we hardly notice any change in the appearance; the solutions appear to have become more viscous, however, for when we shake the solution the air bubbles are held back and ascend slowly. When the sol is not too concentrated, many hours will pass before the $Al(OH)_3$-flakes settle; as their density does not much exceed that of water, they remain quite uniformly suspended in the liquid for a very long time.

Our method of investigation is based upon this fact. When we put the $Al(OH)_3$-sol after the addition of the electrolyte into an Ostwald viscosimeter and determine the rate of efflux from time to time, these rates increase in a

* *Journ. Coll. Sci. Imp. Univ. Tokyo*, 25, No. 8 (1908).
† *Lieb. Ann.*, 89, p. 156 (1854).

regular manner and attain finally a maximum value which corresponds to the complete precipitation. Tables V to VIII and Figs. 1 to 3 will show the time-rate of change. All these experiments were made at 25°.

A question arises as to the relation between the change in the viscosity and the degree of precipitation. In order to inquire into this problem, we completely precipitated sols of different concentrations by means of an electrolyte (solution of potassium ferrocyanide), and we measured the maximum viscosity. It will be recognized from Table I that the augmentation of the

TABLE I.

m.	$\Delta\eta_\infty$ (in Seconds).	$\Delta\eta_\infty / m = \beta$.
0·187	8·0	42·9
0·28	12·0	42·9
0·48	21·2	44·2
1·12	55·6	50·0

viscosity increases in approximate proportion to the amount of precipitated $Al(OH)_3$; in this table m signifies the mass of $Al(OH)_3$ reckoned as grammes of Al_2O_3 per litre, and $\Delta\eta_\infty$ is the difference between the maximum time of efflux and the original rate; $\Delta\eta_\infty / m = \beta$, it will be seen, is practically constant.

In the most concentrated solutions the $\Delta\eta_\infty$ is somewhat too large; the straight-line of the $\Delta\eta_\infty / m$ would by extrapolation yield a value of 48 (instead of 55·6).

Thus we only measure the viscosity of the $Al(OH)_3$-suspensions in their relation to the amount of suspended particles. Our results agree on the

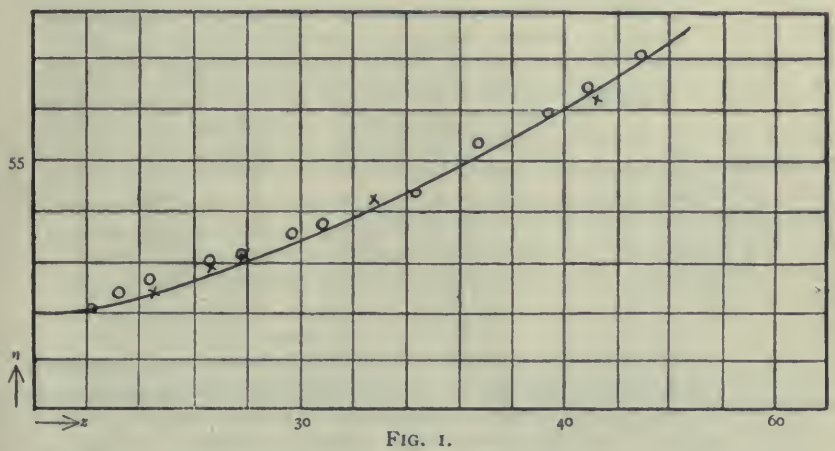


FIG. 1.

whole with those previously obtained. On the strength of theoretical deductions Einstein* has proposed the equation

$$\eta = \eta_0 (1 + \phi),$$

where η is the viscosity of the suspension, η_0 that of the pure medium, and ϕ

* *Annal. d. Physik.*, 19, p. 289 (1906). See also Hatschek, *Kolloid Zeilschr.*, 7, p. 301 (1910).

the volume of matter suspended per unit volume of the medium. In testing this formula Bancelin* arrives at the conclusion that the equation should be transformed into $\eta = \eta_0(1 + 2{\cdot}9\phi)$; the proportionality factor would thus differ from 1, and Einstein proposes after recalculation $\eta = \eta_0(1 + 2{\cdot}5\phi)$. Bingham and Durham† have determined the viscosity of suspensions of kaolin, graphite, etc. Their results are referred to fluidity, and they can be expressed by Einstein's formula only for very dilute suspensions and when the terms of higher order are neglected. Unfortunately, most of their suspensions were fairly concentrated; but so far as their experiments admit of drawing conclusions as to dilute solutions, the proportionality factors seemed decidedly to differ for different materials. The most diluted silver-sols which Woudstra‡ has examined would yield a coefficient of about 1·5.

When we make similar calculations for our experiments, and when we therefore compare the viscosity of the $Al(OH)_3$-suspension with that of pure water, we still find a linear law; but the factor of proportionality is very much larger than in the cases mentioned.

Reviewing all the data, it looks indeed as if a linear law held for the dependence of the viscosity upon the amount of suspended matter at small concentrations, whilst the proportionality factor would vary considerably. The reason may be that Einstein based his deductions on very small rigid spheres, suspended in the liquid, and that this condition of rigidity would scarcely be fulfilled in the case of the $Al(OH)_3$-suspensions, for instance.

Another set of circumstances have to be taken into consideration. It was noticed that the maximum viscosity was *not* independent of the nature of the electrolyte serving as precipitant, though independence might have been expected. Table II will show how large the discrepancies can be; the sol in question contained 0·88 gr. of Al_2O_3 per litre, and the figures indicate the velocities of efflux in seconds.

TABLE II.

Electrolyte.	η_∞.	$\Delta\eta_\infty$.
KNO_3	74	22·0
KCNS	74	22·0
NH_4Cl	77	25·0
K_2SO_4	103·9	51·9
$K_3Fe(CN)_6$	104	52·0
K-salicylate	100·3	48·3

It should be mentioned that in these experiments the sol was precipitated with so concentrated a solution of electrolyte that the maximum viscosity was at once attained and maintained unchanged. An increase in the viscosity with increasing concentration of the colloid, following a linear law, was observed in all cases.

We have not yet been able further to investigate the cause of this peculiarity. The most plausible explanation is that the particles precipitated by different electrolytes are of different nature. Table II unmistakably points

* *C.R.*, **152**, p. 1386 (1911).
† *Amer. Chem. Journ.*, **46**, p. 278 (1911).
‡ *Zeitschr. Phys. Chem.*, **63**, p. 619 (1908).

to a lyotropic sequence of the anions, $NO_3 < Cl < SO_4$, which is likewise met with in hydration. The particles precipitated by univalent anions might possibly be richer in water and hence less viscous than the particles coagulated by multivalent or by organic anions.

It was further found that the maximum viscosity of concentrated sols was decidedly influenced by their mechanical treatment; the viscosity decreased distinctly each time after shaking. Thus the velocity of efflux was, in the case of a sol which contained 1·12 gr. of Al_2O_3 per litre and which was precipitated by $K_4Fe(CN)_6$, reduced from 107·6 to 84·2 seconds. Dilute sols did not display any similar behaviour.

Similar observations had already been made with many sols, above all with emulsion colloids; I will only remind members of some experiments of Biltz's* with solutions of colouring matters. The results once more point to a very close connection between hydroxide-sols and emulsion colloids. The phenomenon may be due to various causes, such as change in the structure of the coagulated particles, their adhesion to the walls.

When we examine to what extent these experiments on the variation of viscosity admit of drawing conclusions as to the degree of precipitation, we may say that the amount of the precipitated particles may, in first approximation, be considered proportional to the increase in viscosity. This statement is, however, only more or less valid as long as the increase in viscosity is not too large, for the value of the maximum viscosity is rather uncertain with concentrated sols on account of its dependence upon the nature of the anions and upon mechanical influences. To render the determination of this maximum as reliable as possible the sol is precipitated, as I stated already, at so high an electrolyte concentration that the maximum value is at once attained and that it remains unchanged, provided the liquid be very little shaken. It should, however, be emphasized that we can also attain the same maximum limit when we precipitate with dilute electrolyte. The following considerations, moreover, depend above all upon experiments in the range of moderate increase of viscosity.

We turn to the curves concerning the rate of coagulation. Fig. 1 illustrates two series of experiments with solutions of NH_4Cl of the same concentration; we recognize that the experiments can easily be reproduced, and that they do not depend on accidental features.

Extensive quantitative investigations of the rate of coagulation were first made by Paine.† He made use of electrically disintegrated copper-sols—more correctly copper oxide-sols; he filtered the precipitated particles and determined analytically the amount of copper remaining in colloidal solution. Now our experiments agree in every point with those of Paine, and this appears remarkable, considering that the two methods and the two sols differed so much. Figs. 2 and 3 reproduce the curves of the rate of coagulation of the $Al(OH)_3$ by NH_4Cl and by K-salicylate at various concentrations. The abscissæ are times, the ordinates velocities of efflux in seconds; the sol contained 0·88 gr. of Al_2O_3 per litre, and the temperature was 25°. Like Paine, we observed a very decided *inflexion* in the curves. Immediately after the addition of the electrolyte the viscosity appears little changed; then it begins to increase suddenly at an accelerated rate and approaches its limit asymptotically.

We might imagine that during the initial period other phenomena took place, *e.g.*, adsorption of the electrolyte by the colloidal particles, and that

* Biltz and v. Vegesack, *Zeitschr. phys. Chem.*, **73**, p. 481 (1910).

† *Proc. Camb. Philos. Soc.*, **16**, p. 430 (1912); *Kolloid Chem. Beihefte*, **4**, p. 24 (1912).

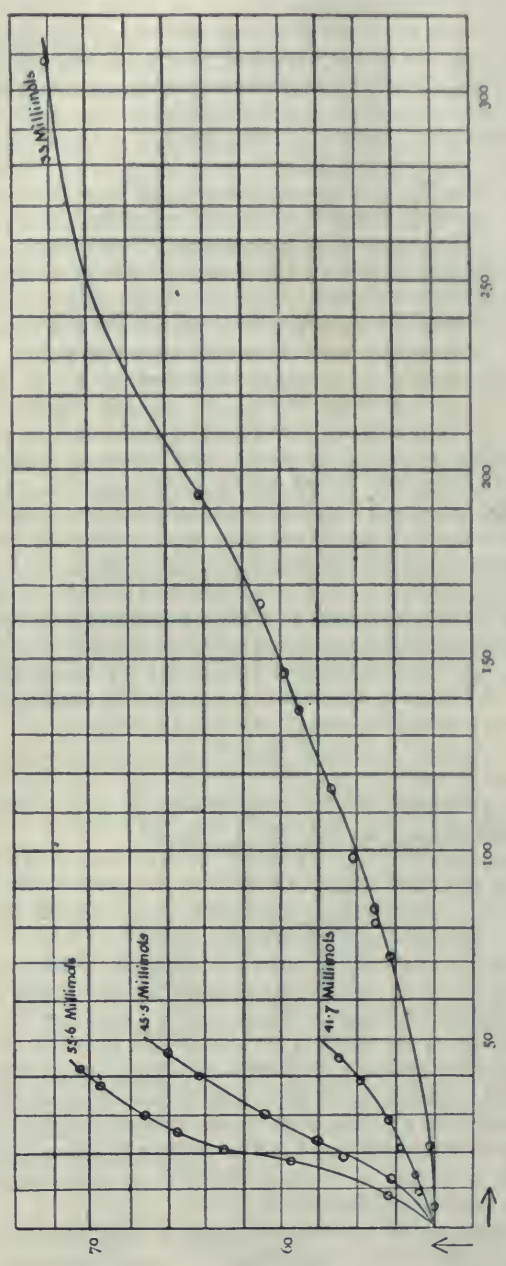

33 Millimols
55·6 Millimols
45·3 Millimols
41·7 Millimols
300
250
200
150
100
50
70
60

FIG. 2.

the precipitation followed afterwards. But Paine has already demonstrated that this assumption cannot be upheld. Quite apart from the well-known fact that the adsorption is generally effected in a very short time, we notice from the curves that the initial period—the incubation period—is strongly and regularly influenced by the concentration of the electrolyte. We recognize from Fig. 2, for instance, that with a concentration of 33 millimol of NH_4Cl per litre—the concentrations are always referred to the state subsequent to the dilution by the sol—there was a change of only 10 per cent in 2 hours, whilst with a concentration of 55·6 millimol the same change was produced in about 12 minutes. The curves are thus entirely of a uniform character, and the initial portion cannot be due to secondary circumstances.

Paine has already pointed out that this character of the curves enables us to understand the existence of an *inferior limit* for the precipitation. If we keep

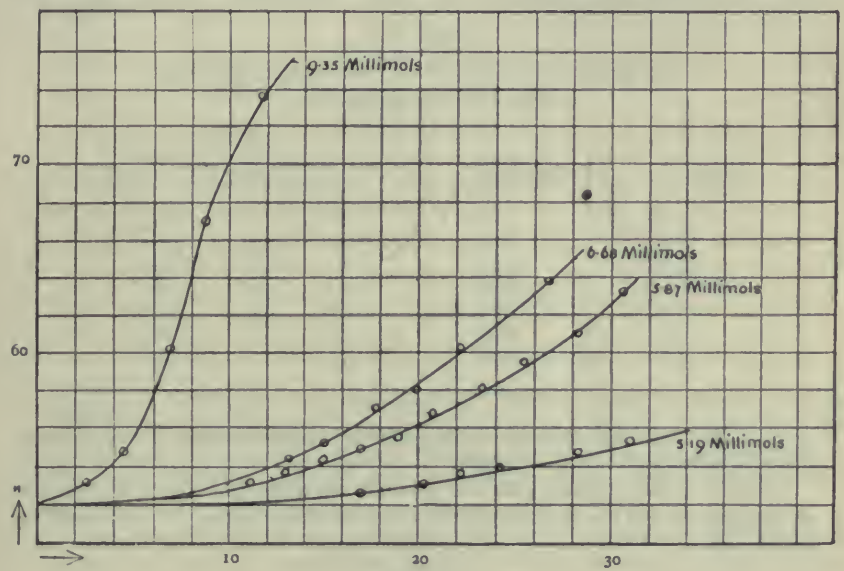


FIG. 3.

below a certain concentration of the electrolyte, the incubation period is practically of infinite length ; within a critical range of concentration we quickly arrive at complete precipitation. We can further conceive how it is that an apparently stable colloidal solution suddenly begins to coagulate : it contains sufficient electrolyte to start with, so that coagulation may set in after a definite, albeit perhaps a very long, period of incubation.

Our experiments were also in good quantitative accord with those of Paine. The latter observed that the curves resulting with different concentrations of the electrolyte were *similar* to one another. Hence, when we compare the periods which correspond to the same degree of precipitation—and thus to the same increase in viscosity—on different concentration curves, the ratio of the periods z will be found to be constant. Table III will exemplify this.

From this constancy we may conclude in the first instance that the point of inflexion is independent of the concentration of the electrolyte, in so far

as the increase of viscosity, *i.e.*, the degree of coagulation, is at this point the same for all curves. The curves Figs. 2 and 3 bring this out very clearly.

We see further that, as Paine has already done, the influence of the concentration of the electrolyte upon the rate of coagulation may be allowed for in calculations. For we deduce the one curve from the other simply by multiplying by a certain factor V, the *factor of the rate of coagulation*, which is manifestly a measure of the effect produced by the change in the concentration of the electrolyte. If we refer this factor to an arbitrary unit rate of coagulation at highest dilution, we find the subjoined table (Table IV) for the K-salicylate.

We see that the factor of the rate of coagulation grows rapidly with an increase in the concentration of the electrolyte, and that is the reason why the precipitative power diminishes so rapidly at small concentration. I might mention that in the experiments with NH_4Cl, in which a rapid precipitation within a quarter of an hour was realized at a concentration

TABLE III.

Precipitation by K-salicylate; concentration 5·87 and 9·35 Millimol per Litre.

Δn.	$Z_{5\cdot87}$.	$Z_{9\cdot35}$	$Z_{5\cdot87}\,Z_{9\cdot35}$
1·2	10·8	2·8	3·85
2·8	17·0	4·6	3·70
4·8	20·9	5·7	3·67
6·0	23·2	6·2	3·87
7·6	25·5	6·8	3·75
9·0	28·0	7·2	3·89
11·2	30·6	7·9	3·87

of 55 millimol, there was no change in the viscosity within 7 hours when the concentration was 20 millimol.

Paine has also proved that the relation between the factor of the rate of coagulation and the concentration of the electrolyte may be expressed by the equation

$$V = Lc^p$$

In this formula c signifies the concentration of the electrolyte in the sol as conditioned by the adsorption equilibrium; we should therefore deduct, from the total concentration as given in Table IV, the amount which has been adsorbed by the coagulated particles. As we did not succeed in making such measurements in a completely satisfactory manner, we have for the present refrained from making this correction and we have simply based our calculations on the total concentration. The L and p are constants; p has in Paine's experiments the value 6. The agreement of our experiments with the equation is shown in Table IV by the V (calculated).

The above will serve to show that our results decidedly confirm those of Paine.

We now pass to some considerations and calculations which go beyond these results. The next problem was evidently to find an equation for the curves of the rate of coagulation. The most desirable thing would, of course, be that our views concerning coagulation were sufficiently precise to base an equation upon them But our knowledge of the precipitation of suspension colloids

is not sufficiently clear yet. We know the following: The adsorption of that ion which carries a charge opposite to that of the colloid particle is of decisive importance for the coagulation, and the large part played by valency and by organic ions may be explained as due to adsorption. We should like to remark that our most recent, yet unpublished researches enable us to assert with certainty that the relation between adsorption and colloid precipitation, developed by one of us* actually exists. We know further that the electric charge of the colloid particles is changed by the adsorption, that the particles are discharged, and that this discharge is important for the coagulation of the particles. We need only point out that according to Hardy,† Burton,‡ and others the suspension colloids are most unstable at the isoelectric point; further that according to Perrin,§ and above all to Elissafoff,|| there is complete parallelism between the precipitative action of electrolytes on colloids and their action in endosmosis and cataphoresis.

One question in particular remains to be answered, however: How is it that the change in the electric charge of the colloid particles causes them to

TABLE IV.

$L = 0{\cdot}0074$; $p = 2{\cdot}998$.

Concentration of the K-salicylate Solution, Millimol per Litre.	V (observed).	V (calculated).
5·19	1	1
5·87	1·7	1·5
6·68	2·0	2·2
9·35	6·3	6·1

coagulate? We might naturally think that differences in the electric charges cause a sorting-out of the particles. Yet we are inclined to suppose in the first instance that this change in the charge affects all the particles uniformly, and we do not at first see any reason for any asymmetry between the particles.

One of us¶ believed to have found a cause for an asymmetrical discharge in the fact that the distribution of the particles towards the ions at the moment of the addition of the electrolyte to the sol will not be entirely uniform, and that these differences between different particles will lead to a non-uniform discharge and to differences of potential between the particles. But Paine has justly pointed out that the variation of the rate of coagulation is too regular to account for the asymmetry merely by so accidental a factor, and our own experiments with $Al(OH)_3$-sol oblige us to concede that this factor can merely be of secondary importance.

On the other hand, a suggestion thrown out by Paine seems to us very happy. He points out that, considering the small size of the colloid particles, we should not presume that the number of ions adsorbed by a particle would remain constant—as would be the case with a large surface. The number of ions might fluctuate about a mean value, and the fluctuations

* Freundlich, *Zeitschr. Phys. Chem.*, **73**, p. 385 (1910); *Kapillarchemie*, p. 345, etc.
† *Zeitschr. Phys. Chem.*, **37**, p. 385 (1900).
‡ *Phil. Mag.* (6) **12**, p. 472 (1906).
§ *Journ. de Chim. Phys.*, **3**, p. 1 (1905).
|| *Zeitschr. Phys. Chem.*, **79**, p. 385 (1912). ¶ *Loc. cit.*, p. 4.

might give rise to changes in the charges and to potential differences between the particles, and thus cause coagulation.

If we once succeed in the mathematical analysis of this asymmetry from the standpoint of molecular-kinetics, we shall be able to explain the course of coagulation and its dependence upon the concentration of the electrolyte.

We have not yet succeeded in accomplishing this mathematically in any reliable manner. We have therefore proceeded in another way, and have attempted to find an empirical equation which would indicate the rate of coagulation, in the hope of tracing the asymmetry back to different factors and obtaining an appropriate expression.

The curves representing the precipitation of $Al(OH)_3$-sol by K-salicylate (Fig. 3) can *not* be reduced to the ordinary equation of autocatalysis of a reaction of the first order : $dx/dz = (k_1 + k_2 x)(1 - x)$, where z is the time, x the amount of precipitated particles which was simply supposed to be proportional to the increase in the viscosity as was explained above (see p. 69). The maximum viscosity increase, *i.e.*, the total amount of colloidal particles, was taken as 1 ; k_1 and k_2 are constants.

An equation corresponding to an autocatalytic reaction of the second order—

$$dx/dz = (k_1 + k_2 x)(1 - x)^2$$

did not meet the conditions either ; yet the discrepancies of the calculated from the observed values were smaller than in the former case. A quadratic relation, in itself theoretically very probable and supported by Paine's work, seemed more likely to prove suitable, therefore. Paine had observed that the rate of coagulation of his copper-sol was a quadratic function of the non-precipitated colloid particles—the term $(1 - x)$ refers to these ; for with different initial concentrations of the sol, the length of the periods within which the concentration of the particles was reduced to a certain fraction of the initial value appeared inversely proportional to the initial concentration. This is theoretically probable, because it reflects the fact that the coagulation should be produced by the attraction between the particles. We may then presume with a certain confidence that the correct equation as to $(1 - x)$ will be of the second order.

We ascertained afterwards that an equation

$$dx/dz = 2kz(1 + bx)(1 - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

represented in a very satisfactory manner the rate of coagulation by K-salicylate. By integrating we obtain—

$$k = \frac{1}{z^2(1+b)} \left\{ \frac{b}{1+b} ln \frac{1+bx}{1-x} + \frac{x}{1-x} \right\} \quad . \quad . \quad . \quad . \quad (2)$$

where b and k are constants.

The subjoined tables show the resulting agreement :—

TABLE V.

Precipitation by K-salicylate. $c = 5{\cdot}19$ *Millimol per Litre.*

z (Minutes).	η.	$\Delta\eta$.	x.	$1 - x$.	k.
0	52·0	—	—	—	—
17	52·9	0·9	0·01863	0·9814	0·00063
20·33	53·2	1·2	0·02485	0·9752	0·00059
22·17	53·6	1·6	0·03313	0·9669	0·00065
24·33	54·0	2·0	0·04141	0·9586	0·00066
28·25	55·0	3·0	0·06212	0·9379	0·00072
33	55·5	3·5	0·07247	0·9275	0·00061
					Mean 0·00064

TABLE VI.

Precipitation by K-salicylate. $c = 5{\cdot}87$ *Millimol per Litre.*

z (Minutes).	η.	$\Delta\eta$.	x.	$1 - x$.	k.
0	52·0	—	—	—	—
10·6	53·2	1·2	0·02485	0·9752	0·00021
12·9	53·8	1·8	0·03727	0·9627	0·00021
15·08	54·5	2·5	0·05176	0·9482	0·00022
17·0	54·8	2·8	0·05798	0·9420	0·00019
18·95	55·6	3·6	0·07454	0·9255	0·00019
20·9	56·8	4·8	0·09938	0·9006	0·00021
23·3	58·1	6·1	0·1263	0·8737	0·00021
25·5	59·6	7·6	0·1573	0·8427	0·00021
28·1	61·0	9·0	0·1863	0·8137	0·00020
30·6	63·2	11·2	0·2319	0·7681	0·00021
					Mean 0·00021

TABLE VII.

Precipitation by K-salicylate. $c = 6{\cdot}68$ *Millimol per Litre.*

z (Minutes).	η.	$\Delta\eta$.	x.	$1 - x$.	k.
0	52·0	—	—	—	—
11·3	53·6	1·6	0·03306	0·9669	0·00025
13·12	54·5	2·5	0·05176	0·9482	0·00028
15·1	55·2	3·2	0·06625	0·9338	0·00027
17·8	56·8	4·8	0·09938	0·9006	0·00028
19·8	58·0	6·0	0·1243	0·8757	0·00028
22·9	60·2	8·2	0·1697	0·8303	0·00028
26·8	63·8	11·8	0·2443	0·7557	0·00029
					Mean 0·00028

TABLE VIII.

Precipitation by K-salicylate. $c = 9{\cdot}35$ *Millimol per Litre.*

z (Minutes).	η.	$\Delta\eta$.	x.	$1 - x$.	k
0	52·0	—	—	—	—
2·75	53·2	1·2	0·02485	0·9752	0·0032
4·55	54·7	2·7	0·05591	0·9441	0·0025
7·0	60·3	8·3	0·1719	0·8281	0·0030
9·0	67·0	15·0	0·3106	0·6894	0·0032
11·7	73·7	21·7	0·4493	0·5507	0·0029
					Mean 0·0030

η_∞ was 100·3 according to Table II, hence $\Delta\eta_\infty = 48{\cdot}3$. The constant b is the same for all the curves; it is deduced from the position of the point of inflexion with the aid of the equation for that point, $d^2x/dz^2 = 0$, when b is treated as an unknown. When we attempt to do this with the equation

$$dx/dz = 2kz(1 + bx)(1 - x)^2,$$

we meet with difficulties. We can easily find b, however, when we start from the equation—

$$dx/2zdz = dx/d(z^2) = k(1 + bx)(1 - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

By solving $d^2x/d(z^2)^2 = 0$, we find the simple expression $b(1 - 3x_{m(x,z^2)}) = 2$, where $x_{m(x,z^2)}$ is the ordinate of the point of inflexion of the (x,z^2) curve, which can easily be measured graphically. The resulting value for b was 4·805.

The constant k depends upon the concentration of the electrolyte and is a measure for it. It is intimately connected with the factor of the rate of coagulation V which we have mentioned, and it will be understood that

$$\frac{V_{c_1}}{V_{c_2}} = \sqrt{\frac{k_{c_1}}{k_{c_2}}},$$

so that $k = \lambda c^q$, where λ and q are in such a way connected with the former constants L and p, that

$$\lambda = hL^2,\ q = 2p, \text{ and } h = \frac{k}{V^2}.$$

Table IX illustrates the agreement between the calculated and observed values of k.

TABLE IX.

Precipitation by K-salicylate. $\lambda = 0{\cdot}4733 \cdot 10^{-8}$; $q = 5{\cdot}913$.

c (Millimol per Litre).	k (observed).	k (calculated).
5·19	0·000064	0·000080
5·87	0·00021	0·00017
6·68	0·00028	0·00036
9·35	0·0030	0·0026

In this case too we should not overlook that the concentration of the solution after the adsorption should be considered rather than the total concentration. The reader will easily be able to convince himself that the other relations between λ, q, L and p are likewise satisfied.

When the experiments are made with NH_4Cl, the formula does not hold quite so accurately, although, *e.g.*, in the experiment with 33 millimol of NH_4Cl per litre (see Fig. 2) the constancy of the k-values was very satisfactory. There appeared to be a general tendency of the initial k-values to be too large. This peculiarity may perhaps be ascribed to the circumstance which, as was pointed out already, favours asymmetry and hence coagulation, that there are initially local differences in concentration owing to incomplete mixing. The relatively high concentrations used in precipitating with NH_4Cl might chiefly be responsible for the accentuated occurrence of this disturbance. It will in any case be necessary to test a large number of electrolytes with respect to their influence on the rate of coagulation.

We may now enquire what we may deduce from our empirical equation (1) $dx/dz = 2kz(1 + bx)(1 - x)^2$ as to the asymmetry of the charges of the colloid particles, which asymmetry, as discussed above, causes coagulation. We may evidently express the rate of coagulation by the general function—

$$dx/dz = k_1 f(U)(1 - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The factor $(1 - x)^2$ of this equation indicates the mutual attraction of the particles, whilst $f(U)$ is to represent the effect of the want of symmetry, and thus of all the factors which call forth or accelerate the coagulation. When we compare equations (4) and (1) we find—

$$f(U) = k_2 z(1 + bx) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and by reference to equation (3) that $k_2 = \lambda_1 c^q$, therefore—

$$f(U) = \lambda_1 c^q z(1 + bx) * \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Equation (6) would indicate a relatively simple dependence of the asymmetry upon various factors : the latter would directly depend upon the amount of precipitated particles, and be simply proportional to the time and proportional to some power of the concentration of the electrolyte. It will be admitted that these conclusions cannot be considered as improbable from the molecular-kinetic standpoint. Thus, for instance, the proportionality to time appears quite possible. The longer the time in which the colloidal particles and electrolyte can act upon one another, the more frequently asymmetrical constellations may arise, which would favour coagulation. That the influence of the electrolyte is proportional to some power of the concentration would tend to suggest that the amount absorbed is the essential factor, and that its influence is exerted in an enhanced degree—the exponent q is very much greater than the exponent $1/n$ of the adsorption isothermal which we have directly measured in a few cases for the sol. This again would not be inconceivable.

It is further noteworthy that the amount of coagulated particles will influence, but not call forth, the asymmetry ; $-f(U)$ does not become zero, when and because $x = 0$. On the other hand $f(U) = 0$ when the concentration c of the electrolyte and the time z vanish ; these quantities thus do not merely influence the asymmetry, but will call it forth.

* The indices of k_1, k_2, λ_1, in the equations (4) to (6), are to indicate that, for reasons which will easily be understood, certain proportionality coefficients have to be introduced when we combine (4) with (1) and with (3).

We hope to have demonstrated by our experiments that the observation of the time-rate of the change in the viscosity of a sol is to a high degree suitable for measuring the rate of coagulation. When this rate is better known—as yet we still need experiments on the influence of temperature and a development of the molecular-kinetic foundations—we shall have elucidated one of the most important phenomena of the chemistry of colloids. This knowledge we shall then be able to utilize for the explanation of complicated processes, as, for instance, the heat coagulation of proteins, in which a rate of colloid-chemical coagulation is combined with a velocity of chemical reaction; the latter has been investigated by C. J. Martin and Harriette Chick.* Above all we shall have to endeavour to resolve the very complicated phenomena of colloids and the still more complicated biological phenomena into their simple chemical, colloidal, and electrical processes, and if possible to investigate these processes separately.

Summary.

1. The velocity of coagulation has been determined quantitatively from the rate of change of the viscosity of $Al(OH)_3$-/sol to which an electrolyte has been added. The results confirm the conclusions at which Paine arrived when experimenting with copper-sol by other methods:—

(*a*) The curves relating to the degree of precipitation and to time have a point of inflexion; immediately after the addition of the electrolyte there is no change of the sol, or only a very small change.

(*b*) The curves resulting with different concentrations of the electrolyte are similar to one another. It follows that the point of inflexion corresponds to the same value of the increase in viscosity. Further, we can deduce one curve from the other by multiplying the times of the various degrees of precipitation by a certain factor—the *factor of the rate of coagulation*; we can thus find the other times for corresponding degrees of precipitation.

(*c*) The factor of the rate of coagulation V is connected with the concentration c of the electrolyte in the solution by the equation

$$V = Lc^p,$$

where L and p are constants; the value of p ranges from 3 to 6.

(*d*) The shape of the curves and the high numerical value of the coefficient p readily account for many peculiarities in the precipitation of colloids; for instance, the lower limit of precipitation and the frequently observed sudden coagulation of a sol, etc.

2. In extension of the researches of Paine, it is shown that the curves of the rate of coagulation by potassium salicylate can be well expressed by the differential equation

$$dx/dz = 2kz\,(1 + bx)\,(1 - x)^2,$$

which integrated yields—

$$k = \frac{1}{z^2(1+b)}\left\{\frac{b}{1+b}\,ln\,\frac{1+bx}{1-x} + \frac{x}{1-x}\right\},$$

in which x is the amount precipitated (counting the total quantity as 1), z signifies the time, and b and k are constants, b being independent of the concentration of the electrolyte, and a function of the x for the point of inflexion, and k being a function of the concentration of the electrolyte.

* *Journ. of Physiol.*, 40, p. 404 (1910), 43, p. 1 (1911), 45, pp. 61 and 261 (1912).

3. The constant k of the rate of coagulation is connected with the concentration c of the electrolyte by the equation

$$k = \lambda c^q ;$$

this equation and the equation of Paine are interconnected by the relations $\lambda = hL^2$ and $q = 2p$; the proportionality constant h is defined by $h = k/V^2$.

4. The maximum viscosity of an $Al(OH)_3$-/sol which is completely precipitated by the addition of an electrolyte, increases proportionately to the amount of colloid particles in the sol. This is in accordance with previous experiments on suspensions and emulsions.

5. The maximum viscosity is to a certain degree dependent upon the nature of the precipitating electrolyte ; the results recall the lyotropic series in so far as the viscosity is smaller with the anions NO_3, CNS than with sulphate, succinate, etc.

6. The maximum viscosity of concentrated sols is further distinctly influenced by mechanical effects, shaking, etc.

THE GENERAL THEORY OF VISCOSITY OF TWO-PHASE SYSTEMS.

Mr. Emil Hatschek read a Paper on "The General Theory of Viscosity of Two-Phase Systems."

Notwithstanding the importance of this physical constant, and the fact that the literature of the subject contains many records of viscosity determinations, and of attempts to explain changes in heterogeneous systems on the basis of such measurements, the author is not, with one exception, aware of any attempt to treat the internal friction of such systems mathematically beyond two papers (1) published by him in 1910–11. The reader is referred to these for full details, only the main features and the results being reproduced in the present paper.

The first paper deals with the viscosity of a liquid, in which are suspended undeformable spheres of small diameter, which occupy in the aggregate only the smaller part of the total volume of the system, say not more than 40 per cent. of it. Fig. 1 shows such a system diagrammatically, the layer of liquid being contained between two parallel plates, one of which is stationary, while the other is moved in itself with a constant velocity. It is obvious that the liquid at the upper pole of each spherical particle moves with a somewhat greater velocity than at the lower pole, which is equivalent to a translatory movement of the particles with a velocity equal to half the difference of the two velocities prevailing at the two poles. By carrying through the calculation on the basis of this reasoning, an expression is obtained for the viscosity of the whole system. If we call—

η viscosity coefficient of liquid (or continuous phase),

f the ratio $\dfrac{\text{Total volume of particles (or disperse phase),}}{\text{Total volume of system}}$

η^1 viscosity of system,

the latter is given by the formula—

$$\eta^1 = \eta\,(1 + 4{\cdot}5f) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The radius and the distance of the particles do not appear, and the formula accordingly states that *the viscosity of a system of undeformable particles suspended in a liquid is independent of the size of the particles and is a linear function of the volume of disperse phase only.* The only qualification necessary is the following: Stokes's formula is employed in the calculation, and the formula (1) accordingly holds good only between those limits between which Stokes's formula holds good.

An almost identical result had been obtained by A. Einstein (2) in 1906. This paper deals with the determination of Avogadro's number by thermodynamical methods, and incidentally Einstein obtains the following expression

(using the same symbols as before) for the viscosity of a liquid with small spherical particles suspended in it—

$$\eta' = \eta (1 + f) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The formula is therefore functionally identical with the author's formula (1), and only differs in the numerical constant, which is 1 instead of 4·5.

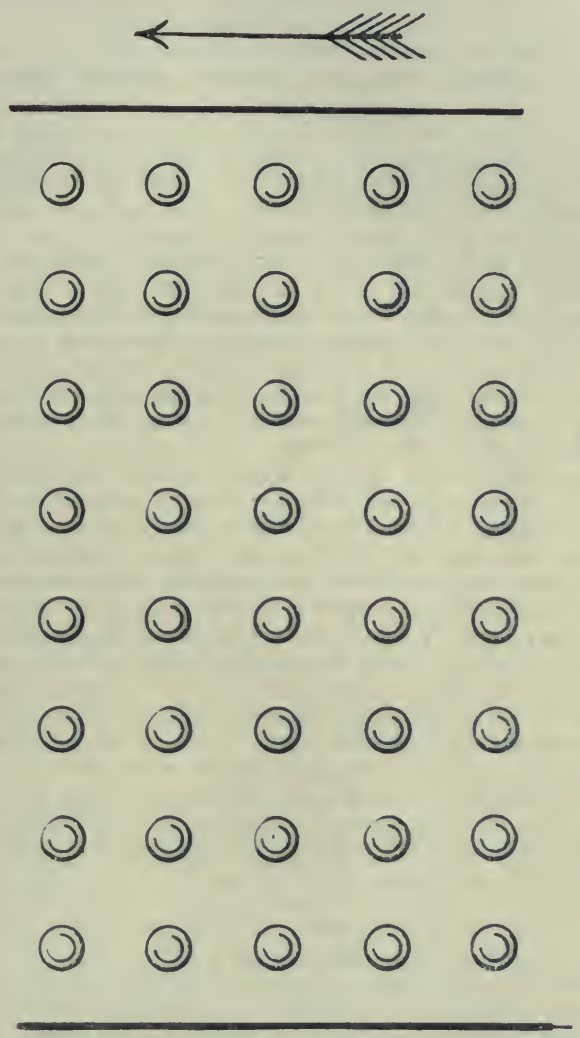


FIG. 1.

Einstein's formula was checked experimentally by M. Bancelin in 1911 (3). Certain discrepancies led Bancelin to correspond with Einstein, and the latter revised his calculations and altered the numerical constant from 1 to 2·5. Bancelin used spheres of gamboge made according to Perrin's method (precipitation of an alcoholic solution and fractionation by centrifuging) and found that the *viscosity of a suspension of such particles in water*

was independent of the diameter of the particles and increased in linear ratio with the volume of disperse phase, up to 3 per cent. of the latter. The constant however was found to be *2·9*. The volume of disperse phase was determined by weighing, a method open to certain objections to be dealt with further on.

The author's formula was tested by Wm. Harrison (4) with suspensions of starch granules of very different origin, and therefore diameter, in water. This investigator found *an increase in viscosity independent of the size of the particles* (*i.e.*, the same increase with all starches used) *and in linear ratio to the* volume of disperse phase present, with a numerical constant of *4·75 instead of 4·5*. He also determined the *true volume* of disperse phase; weighing being out of the question, in view of the swelling of the starch, he centrifuged the suspensions in graduated tubes, and read the volume of disperse phase directly. The volume thus determined is no doubt somewhat too large, on account of the probable voids between the grains, but is certainly directly proportional to the true volume. Harrison found the formula to hold good up to 30 per cent. of disperse phase.

The systems just referred to are of course suspensions with a disperse phase consisting of particles very much larger than those which occur in colloidal solutions of the suspensoid class. A number of viscosity determinations on such sols are also to be found in the literature. In many cases these have been made on systems of the low degree of concentration which is generally characteristic of such sols, so that the variations in viscosity which have been measured are frequently very little in excess of the errors of experiment. A series of determinations free from objections —except certain difficulties in dealing with ultra-microscopic particles which are inherent—has recently been published by Sven Oden (5). The sols used were sulphur sols, made by Svedberg and Oden's method of fractionated coagulation, which permits the preparation of sols having particles of uniform size, and of considerable concentration, up to 50 per cent. by weight or about 25 per cent. by volume. The measurements show two important divergencies from the theoretical result: (1) the viscosity above a certain concentration grows more rapidly than in linear ratio, and (2) the viscosity of sols containing smaller particles is, for equal weights, higher throughout than that of sols with larger particles.

At the present moment there appears to be no satisfactory explanation of the first discrepancy. It is at least possible that it may be in part due to the use of the ordinary capillary viscometer, and measurements at much lower rates of shear in a different apparatus are therefore required to settle this point. Such measurements and the apparatus used will be referred to further on. As regards the higher viscosity of more highly disperse systems, *i.e.*, such containing smaller particles, the case is different, and several points of high theoretical interest are raised by it. It must be remembered that all that is definitely known is the *weight of disperse phase*, whereas the formula, or any conceivable mathematical expression, contains the *volume*. As regards this, certain well-known assumptions are always made in ultra-microscopic determinations, viz., that the particles are of a simple geometrical shape, necessarily assumed to be the same for large and small particles, and that the density of ultra-microscopic particles is the same as that of substances in bulk. The further assumption that, for equal weights, disperse systems of different degrees of dispersity also contain equal volumes, is a necessary corollary of the previous ones.

As is well known, neither of the two assumptions is capable of proof. The examination of microscopic—as compared with ultra-microscopic—

precipitates shows, however, that particles of different sizes may, and very generally do, have very different shapes, and therefore very different coefficients of friction or resistance when moving in a liquid.

This question, which may well arise in the case of many sols, is however practically eliminated in that of the sulphur sols examined by Sven Oden, as a spherical shape is reasonably certain in these sols. Nevertheless, there are extremely strong grounds for the view that the *effective volume* is not constant, *i.e.*, simply proportional to the weight, for different degrees of dispersity. It is quite generally supposed that such particles as are here considered are surrounded with an adsorption envelope, which moves with them, so that the effective volume of the particle is the sum of two factors: volume of actual disperse phase (probably, but not necessarily proportional to the weight) plus volume of adsorption envelope.

The aggregate volume of these adsorption envelopes is the product of their thickness into the total surface of the disperse phase. If the thickness is constant for a given system, *it follows at once that the aggregate volume of adsorption envelopes and therefore the effective volume of disperse phase increases with increasing dispersity*, as found by Oden. The two sols investigated by the latter were a sol with submicroscopic particles of 100 $\mu\mu$ diameter, determined ultra-microscopically in the usual way, and an amicroscopic sol with particles estimated at 10 $\mu\mu$ diameter. It is of course possible to calculate from these data and the observed ratio of the two viscosities the thickness of the adsorption envelope. This has been done by the author (6), and the figure found is 0·87 $\mu\mu$. The value has nothing inherently improbable, and the only striking feature is that so slight an envelope is sufficient to increase the effective volume so considerably.

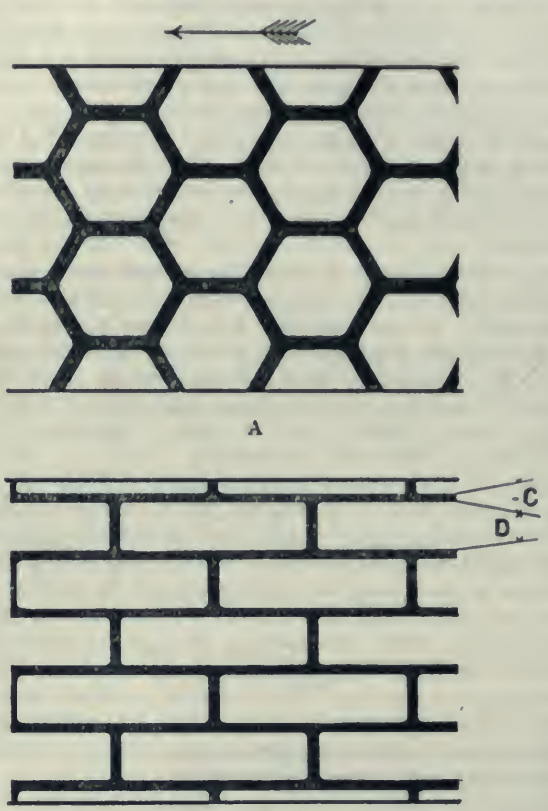
The adsorption envelope, while it accounts perfectly for the greater viscosity—given equal weights of disperse phase—hardly explains the other discrepancy between the theoretical conclusions and the observed results in sols, viz., the more than linear increase of the viscosity with growing concentration. Several explanations, all tentative, suggest themselves. One is the possibility of particles impeding one another at much lower concentrations than those assumed, while the formula disregards mutual disturbances. Another is the assumption that a mere translatory motion of the particles in the direction of shear does not fully represent conditions, as an additional rotary motion of the former is quite conceivable: this would call for further energy, which would increase with decreasing distances between particles and accordingly with increasing concentration.

It finally appears possible, as already mentioned, that the capillary viscometer may give rise to disturbances, and it appears at least eminently desirable to determine the viscosity of heterogeneous systems by some alternative method—even if this should lack the convenience of the transpiration method. For this purpose the author has adapted the apparatus used by Couette (7) for determining the viscosity of water at low rates of shear. Owing to the very great difficulties experienced in bringing the apparatus to its present convenient form, and to pressure of other work, only a few results are available at the time of writing, which will be given later. The method appears even more essential for obtaining an insight into the mechanism of the processes in a system of two liquid phases, such as we shall have to consider next, and the description of the apparatus therefore follows the theoretical consideration of this class, the emulsions and emulsoids.

The systems considered so far all contain a disperse phase which is not deformable, and which amounts to considerably less than half the total volume of the system. It is by no means necessary that the disperse phase

should be, in bulk, a solid substance: small globules of liquid widely separated would undergo no appreciable deformation during shearing, and the whole reasoning would apply to them equally.

If we are therefore to account for the peculiarities, and more especially the high viscosities, of systems like emulsions, which are known, and emulsoids, which for many cogent reasons are considered, to be systems of two liquid phases, we have to make a further assumption, namely that *the disperse phase occupies a considerable part, say at least one half and generally very much*



A

B

FIG. 2.

more, of the total volume. It is obvious that such phase ratios are possible with two liquid phases, and equally obvious that the system must have a perfectly definite geometrical structure.

If we imagine a system of spheres in a given space, and let their radius or their number increase until they are in closest contact, *i.e.*, until each sphere touches twelve others, the aggregate volume of the spheres is 74·04 per cent. of the total space occupied. The twelve points of contact are the centres of the faces of a dodecahedron (two different dodecahedra are possible, into which question it is not necessary to go), and, if the volume of the spheres is increased further, flattening must take place and the faces of the dodecahedron be developed more and more.

While the author has found a general treatment of the viscosity of a system of two liquid phases impossible, it is comparatively easy to proceed

synthetically from the stereometric considerations just developed. Fig. 2 A shows diagrammatically a film of such a two-phase system, the disperse phase being shown white and the films of continuous phase black. As explained, the former assumes necessarily the shape of dodecahedra, the hexagons being sections through these. If the system is now sheared, the polyhedra must slide over one another, and in a certain position the system must assume the altered shape shown in Fig. 2 B. A simple calculation, for which the reader is referred to the original paper, will show that such rectangular prisms fill space again continuously and are therefore possible.

If shearing is continued, the system has of course a tendency to assume its original shape. The factor tending to bring about this return is the interfacial tension between the two phases, which would reduce the interface to the minimum possible in the circumstances, *i.e.*, to the polyhedral shape. This tendency, however, is counteracted by the viscosity of both phases, principally by that of the disperse phase, and it is therefore quite possible to conceive that, *above a given velocity of shear, there may not be time for this return to the polyhedral shape and that the system would remain as shown in Fig.* 2 B.

In that event it is obvious that *shearing only takes place in the horizontal films of continuous phase*, and it is a simple matter to calculate the work done on this assumption. It is also obvious that neither the interfacial tension (which has not time to act) nor the viscosity of the disperse phase enter into the calculation, which is given *in extenso* in the original paper. The formula finally obtained, if the viscosity of the continuous phase is taken as unity, is the following—

$$\eta = \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the symbols mean :—

η = co-efficient of viscosity of system,

$$A = \text{ratio} : \frac{\text{Volume of system}}{\text{Volume of disperse phase}}.$$

The curve corresponding to the above equation is shown in Fig. 3, and the similarity to the concentration-viscosity curves obtained with a number of sols, such as caseinogen, rubber, nitrocellulose, etc., is striking without detailed comparison.

The question naturally arises at once, whether the assumption of a minimum or critical velocity of shear is tenable, *i.e.*, whether shearing under ordinary conditions does proceed with such a velocity that the conditions on which the formula is based arise. On the basis of the material available this question can unhesitatingly be answered in the affirmative. The rate of shear in the usual method, transpiration through a capillary, appears far in excess of the minimum, *i.e.*, no anomalies can be observed. Even the very low rates of shear used in the Couette apparatus appear sufficient to bring about the stable condition of stress postulated in many cases.

As regards the application of the formula, a distinction has to be made. In emulsions, in the strict sense of the word, it is of course possible to determine the volumes of both phases, either by using known amounts of them in preparing the emulsion, or by breaking up an emulsion of unknown composition and measuring the resulting two phases. Experiments have been made with coarse emulsions of ordinary paraffin oil in ¼ per cent. soap solution,

prepared by the author's method. The phase ratio was determined from the finished emulsion by breaking up with dilute hydrochloric acid. A 50 c.c. burette is filled up to the fifty mark with dilute acid, and then to the zero

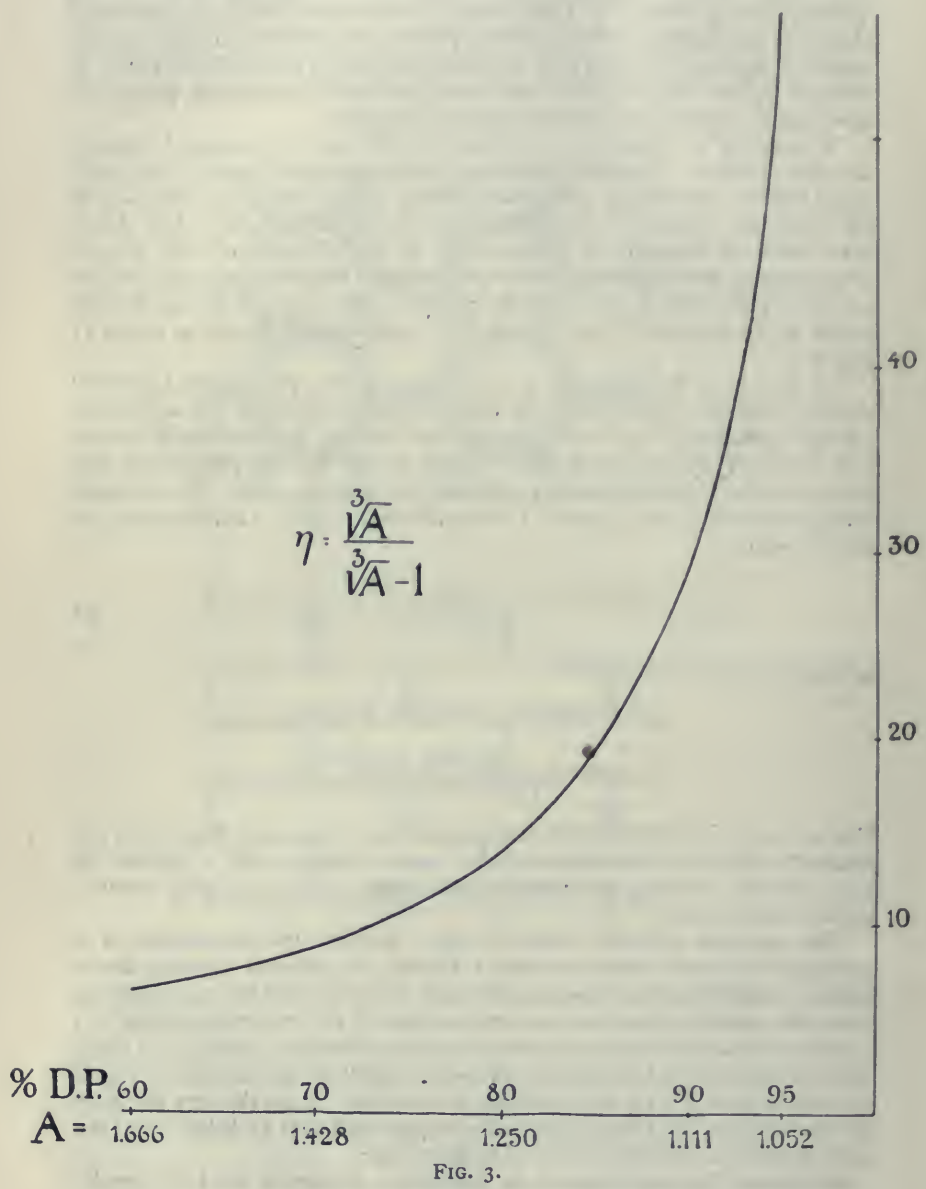


FIG. 3.

mark with 50 c.c. of emulsion. Mixing at once causes breaking up, and after separation the volume of oil can be read off directly. The results are given in Table II and show a very satisfactory agreement.

With emulsoids the case is somewhat more complicated. As is well

known, the sol of an emulsoid, say gelatine or silicic acid, must be assumed to consist of two liquid phases, the disperse phase consisting of droplets of what may roughly be called a hydrate or solvate of the dissolved substance, *i.e.*, composed of the latter and a certain amount of the solvent definitely associated with it. This amount is unknown, and the volume of the disperse phase is obviously equally so. There is accordingly no possibility of applying the formula to such systems unless we make some assumption with regard to the volume of disperse phase, or rather with regard to *the relation of this volume to the weight of substance dissolved*, the latter being the factor usually known.

The simplest assumption, and one, moreover, in entire accord with what we know of the closely related phenomenon of "swelling," is that, at any given temperature, a definite weight of substance takes up a constant amount of solvent to form together with it the disperse phase, or, in other words, that at any given temperature *the volume of disperse phase is a constant multiple of the volume—or weight—of the dissolved substance.* Thus, 1·4 gr. of gelatine, *i.e.*, 1 c.c., might conceivably at a certain temperature take into the disperse phase say 10 or 15 c.c. of water, *i.e.*, 1·4 gr. would form 11 or 16 c.c. of disperse phase.

This assumption can obviously be tested by experimental data. From the known viscosity of a system we can immediately calculate the phase ratio, by the following formula, which is a transformation of (3) :—

$$A = \left(\frac{\eta}{\eta - 1}\right)^3 \quad \ldots\ldots\ldots\ldots \quad (4)$$

A is the ratio $\frac{\text{Total volume}}{\text{Volume of disperse phase}}$. If the amount of dissolved substance is, as is usually the case, given in per cent., this is also a ratio with the same numerator, viz.: $\frac{\text{Total volume}}{\text{Dissolved weight}}$, and, if our assumption is correct, there must accordingly be *a constant ratio between the two, i.e.*, the phase ratio must be a constant multiple of the percentage contents.

Various experimental data have been examined in this sense, and the results are shown in Table I. Column I shows the weight dissolved in per cent.; II, the measured coefficient of viscosity; III, the ratio A calculated from the latter by formula (4); IV, the corresponding ratio : total volume : weight of dissolved substance, and finally, V, the ratio of III and IV, which, according to the assumption, should be constant.

It will be seen that this constancy shows itself satisfactorily between fairly wide limits of concentration. With caseinogen, for instance, 1 gr. of dissolved substance produces approximately 9·5 c.c. of disperse phase, or 1 c.c. (density about 1·3) 12·3 c.c. of disperse phase. The reason why there are discrepancies at lower concentrations is also obvious. 4·35 gr. of caseinogen would only make about 41 per cent. of disperse phase, that is, less than one-half of the total volume. The structure on which the formula is based cannot yet arise at this ratio, and the system cannot therefore conform to it. As a general conclusion, thoroughly confirmed by experience, the emulsoid character, *i.e.*, the very rapid rise of viscosity with concentration, can, even with typically emulsoid substances, *show itself above certain concentrations only:* the dissolved substance plus the solvent associated with it must occupy more than about 50 per cent. of the total volume. Until this happens, the ratio between viscosity and amount of dissolved substance is approximately linear. This shows itself strikingly in all published viscosity curves, but the percentage at which the characteristic rapid rise of vis-

cosity sets in varies enormously in different substances, and is a measure of their "emulsoid" or "lyophilic" properties. With caseinogen it begins at about 5 per cent., with glycogen about 25 per cent., while indiarubber solutions show extremely rapid rises at concentrations above the low limit of 0·4 or 0·5 per cent. From figures given by Schidrowitz and Goldsborough the author calculates that, in forming the disperse phase, rubber takes up 70 to 100 times its own volume of solvent—a figure which is not surprising to those familiar with the preliminary swelling of rubber in its solvents.

Even more than in the case of suspensions, it appears desirable to study the viscosity of emulsions in some way which permits variations *in the rate*

TABLE I.

Percentage by Weight of Dissolved Substance.	η — Coefficient of Viscosity; Water at same Temperature being taken at Unity.	A — Total Volume / Volume of Disperse Phase calculated from Formula 4.	A' — Total Volume / Weight of Dissolved Substance (100 : Percentage).	Ratio $\frac{A'}{A}$ which should be constant.
Glycogen Sol (F. Botazzi and G. d'Errico.) (10)				
20	3·548	2·685	5·00	1·862
25	4·548	2·108	4·00	1·897
30	7·370	1·525	3·33	2·184
35	12·220	1·292	2·85	2·212
40	20·550	1·161	2·50	2·155
45	62·000	1·050	2·11	2·010
Casein (Sodium caseinogenate) Sol (H. Chick and C. J. Martin.) (11)				
4·35	3·37	2·860	22·99	8·040
6·05	6·12	1·715	16·53	9·638
7·06	8·48	1·457	14·17	9·722
8·49	13·66	1·256	11·78	9·377
9·39	23·72	1·138	10·56	9·358

of shear. The latter cannot be altered in the capillary viscometer, as the velocity of flow is settled by the dimensions of the capillary, which are in turn fairly strictly defined by the necessity of avoiding turbulent flow. Such experiments have been made by Garrett (8) on sols of silicic acid, albumen and gelatine: the method employed was the determination of the decrement of the oscillations of a disc submerged in the liquid. Apart from the complicated mathematical treatment necessary, this procedure possesses the grave drawback that the velocity of shear is different at every radius of the disc. While this is no objection in the case of homogeneous liquids, it tends to obscure still further the questions which arise in the investigations of heterogeneous systems, which may conceivably have viscosities either constant

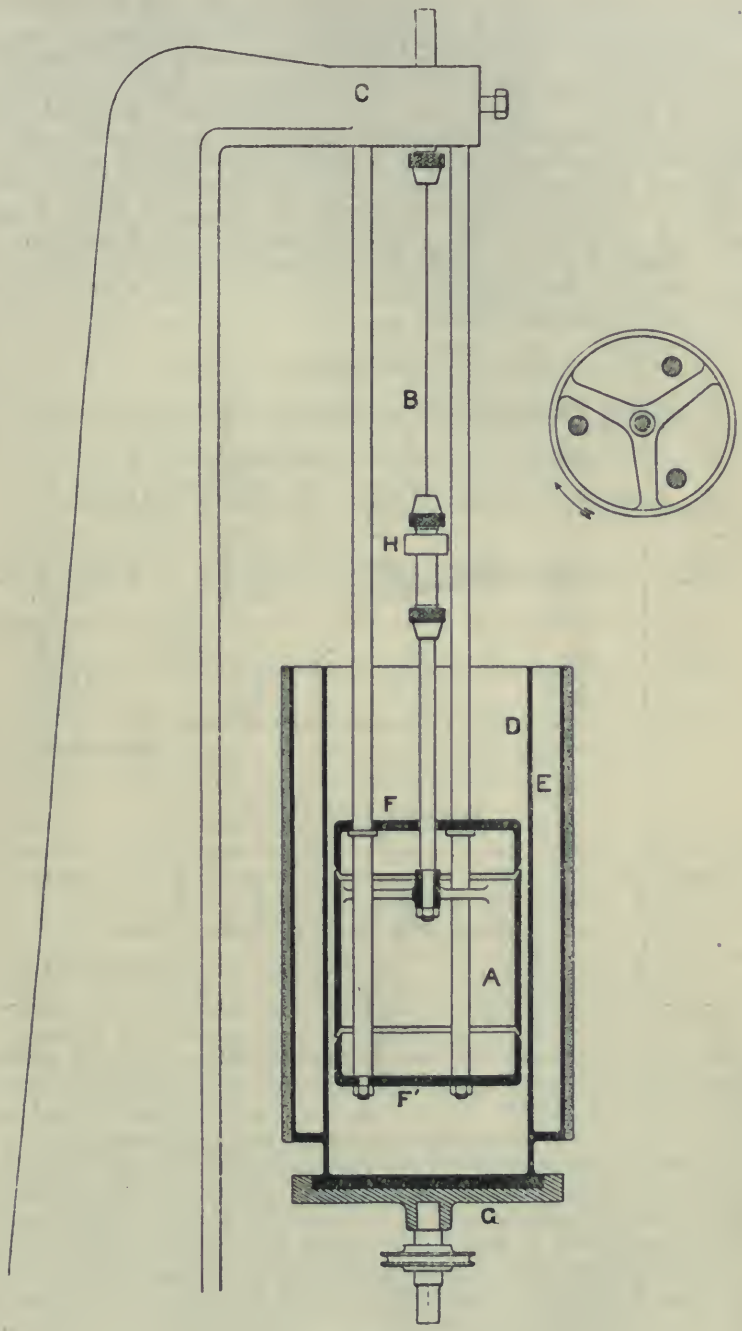


FIG. 4.

only above certain critical velocities, or altogether inconstant, *i.e.*, the viscosity might even be a function of the velocity of shear throughout.

These objections are avoided in Couette's apparatus, the form of which finally adopted by the author is shown in Fig. 4. A hollow cylinder A, which is open and bevelled at the ends, is suspended by a wire B from a heavy bracket C, provided with levelling screws (not shown). This cylinder A is coaxial with an outer cylinder D, which is provided with a water jacket E covered with insulating material. Two short guard cylinders, F and F' —closed at one end—are placed opposite the open ends of the cylinder, leaving a clearance of about 2 mm. between the bevelled surfaces. The outer cylinder D rests on a table G, which can be rotated by suitable gearing. The suspended cylinder A is provided with a mirror H, and its deflection read by scale and telescope.

TABLE II.

VISCOSITY DETERMINATION BY MEANS OF COUETTE'S APPARATUS.

System: Emulsion of Paraffin in Soap Solution.

A. *Viscosity of Continuous Phase:* 0·75 *per cent. Soap Solution.*

Zero.	Reading.	Deflection (Reading minus Zero).	Time per Revolution in Secs.	Product of Time and Deflection, *i.e.*, Rel. Viscosity.
230	266	36	3·8	136·8
,,	271·5	41·5	3·2	132·8
,,	282	52	2·65	137·8
				Mean 135·8

B. *Viscosity of Emulsion.*

29	46	17	96	1632
,,	48	19	83	1577
,,	53	24	67·5	1620
				Mean 1609

When the outer cylinder is filled with a liquid and rotated, the inner cylinder A is deflected, owing to the viscosity of the cylindrical layer of liquid between A and D. The two guards F and F' keep the liquid in the interior of A entirely at rest and eliminate the very complicated effect of the ends, which arises where a closed suspended cylinder is used, as has been done by some observers. It has been shown by Couette and others (9) that the rate of shear is practically uniform in the cylindrical layer of liquid, and that the couple tending to deflect the cylinder A is: viscosity × velocity × an apparatus constant. For a given wire, therefore, assuming the viscosity (as has been shown to hold good for water) to be independent of the rate of shear, the deflection divided by the angular velocity is a constant. It is more convenient, especially for the low velocities to which the apparatus particularly lends itself, to use the product: deflection × reciprocal of velocity, *i.e.*, time taken for one revolution. For relative determinations

the apparatus can be gauged with water at a definite temperature exactly like the capillary viscometer, *i.e.*, the above product is determined. For the same wire, these products for two different liquids are in the ratio of the viscosities, and the specific gravity does not, as in the capillary apparatus, enter into the calculation.

The sensitiveness of the apparatus may be pushed to any desired degree, by using thin wire and a distant scale. The time per revolution is determined by stop watch, by observing the passage of a mark on the cylinder through some non-parallactic sight, of course counting an appropriate number of revolutions. The lowest angular velocity used by the writer so far has been about 3° 38′ per second, viz., one revolution in 99 seconds.

As a first instance of measurements by this apparatus may be mentioned the determination of the viscosity of an emulsion referred to above. This was an emulsion of ordinary lamp paraffin in a ¾ per cent. soap solution, prepared by the author's method (12). This emulsion is fairly coarse, and contains even macroscopic oil globules, so that the use of the capillary viscometer is impossible. (N.B. This has been tried, but with a great range of instruments it was impossible to obtain concordant readings.) The full data are given in the Table I already referred to above.

If the viscosity of the continuous phase is taken as unity, the viscosity η of the emulsion is 1609 : 135·8 = 11·85.

The ratio $A = \frac{\text{Total volume}}{\text{Volume of disperse phase}}$ calculated from formula (4) is accordingly $A = \frac{11{\cdot}85}{10{\cdot}85} = 1{\cdot}302$.

The volume percentage of disperse phase is therefore 100 : 1·302 = 76·7 per cent.

Fifty c.c. of the emulsion was broken up by hydrochloric acid and gave 10·1 c.c. of water and 39·9 c.c. of oil, or 79·8 per cent. of the latter, a satisfactory agreement with the calculated value of 76·7 per cent.

Further work on emulsoid sols is in progress, but the results must be reserved for a future communication. It is however possible to state already that investigation, particularly on gum arabic and gelatine sols, shows that these possess different viscosities at different rates of shear below certain limits. The need of *kinetic methods*, so strongly emphasized by Dr. Ostwald, is equally pronounced in this particular direction. The capillary viscometer only furnishes points, *i.e.*, the viscosity of a given system at given temperatures, and at *those velocities of shear which establish themselves automatically in conformity with the dimensions of the apparatus* and the gravity of the liquid. To gain an insight into the *mechanism* of the viscosity of heterogeneous systems, something more is wanted, viz., investigation at different rates of shear to be altered at will.

In conclusion, the author may perhaps be permitted to express the hope that the theoretical and experimental study of the viscosity of heterogeneous systems may ultimately furnish a starting-point for a general theory of the viscosity of homogeneous systems. The term "homogeneous" is after all only relative, and a solution containing hydrates with many molecules of water may quite probably be treated by the same mathematical methods as similar systems containing microscopic or ultra-microscopic aggregates.

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DISCUSSION.

The subject was then thrown open for general discussion.

Dr. S. B. Schryver: I wanted to call your attention to a somewhat different aspect of viscosity to those which have been discussed for the most part to-day, and that is the influence of the viscosity of the dispersion medium on the capacity for producing dispersion. My interest in this question was attracted by some colloidal reactions of the protein derivatives; in the first case, with a reaction between formaldehyde and Witte's peptone, you get a precipitate formed, which is inhibited by the presence of certain salts, and if you titrate such a mixture with standard alkali you find that whether you get a precipitate or not the formaldehyde has entered into reaction (by Sörensen's titration method). The most reasonable explanation of the action of salts in such a case seems to be that they inhibit the formation of some complex molecule. We know from the work of Schiff that formaldehyde derivatives are capable of forming very complex molecules by the union together of two molecules and perhaps scission of the elements of water, and it seems to me that the most reasonable explanation of a salt action in this case is that the more complex molecules in the Witte peptone mixture which were capable of forming this precipitate had adsorbed the salts from solution and in this way had inhibited the big molecules from combining together to form still larger molecules. And during a quantitative investigation of the action of these salts my attention was called to the great analogy between the inhibitory action of the various salts and their capacity for producing a dispersion of the globulins. I need not go into the details of this, but my idea was that the globulins differ from the albumins in the fact that they are probably double molecules which, in the presence of water, undergo a certain amount of hydrolytic dissociation, and that in the presence of salts, as the molecules dissociated, so they adsorb salts from solution and so the hydrolytic dissociation could proceed further, and that in this way you could explain the peculiar action of salt solutions in producing a solution of globulin. However, I do not want to go in great detail into this point now. I set about to try and ascertain the properties of the salts to which inhibition of the precipitation of Witte's peptone by formaldehyde and the dispersion of the globulins is due. The most obvious thing to investigate in this respect was the surface tension of the solution. One might imagine that those salts which produce the greatest lowering of the surface tension of the solution would be most readily absorbed, and would also inhibit the formation of formaldehyde and Witte's peptone precipitate, and produce a dispersion of the globulins. The salts I took are divided into two series. Those on the Table (shown on the screen) are the surface tensions measured taking water as unity. The inorganic salts for the most part increase the surface tension of water, whereas a considerable number of the organic salts considerably diminish that surface tension. Now I investigated the action of these various salts on the dispersion of the globulins. I used for this purpose an optical method of measurement, and in the Table (shown on the screen) you see the amount of salt necessary to produce a definite grade of dispersion with a given globulin solution (a solution of about 1·8 per cent.). If you look at those two series of salts, you will see that the amount necessary to produce a given dispersion diminishes as the surface tension of salt diminishes, going from 38·5 for sodium chloride down to 15·5 c.c. for sodium sulphocyanide. I am confining my remarks

entirely to sodium salts. Now look at the series of organic salts which are also placed in diminishing order of surface tension. You will find, with the exception of the sodium formate, the more the salt solution lowers the surface tension the less of that solution is found necessary to produce a definite rate of dispersion.

Observe now another series with another suspension only containing the organic salts. You will notice that the inorganic salts have quite a different action to the organic salts. You will find with the organic salts you require very much less to produce a given dispersion than you do with the organic salts the solutions of which have the same surface tensions, and I tried to think out what could be the possible difference between those two series of salts. As a matter of fact, one main difference is the difference in their viscosities. The organic salt solutions are, as a general rule, very much more viscous than the inorganic salts, and it occurred to me that this was possibly the reason why the organic salts had smaller dispersion capacity than the inorganic salts. I also tried to see how the salts acted when applied to systems which contained not colloids but molecular dispersed particles, and I tried to see how the solubility of various crystalline substances in these salt solutions was affected. I took a large series of crystalline substances, the most interesting of which, perhaps, were leucine and phenylalanine (which were synthetically prepared, optically inactive substances), on account of their chemical analogy with the proteins, and you find there you get the same order with regard to solubility of these crystalline substances as you get for the proteins and more complex substances. And it seems to me, therefore, that the solubility of crystalline substances, and the dispersion of colloids, is affected mainly by two properties—namely, in the first place, the surface tension, and secondly, the viscosities of the solutions. I have ventured in my Paper to suggest that the action of viscosity may be explained by the formation of a diffusion area round one of the phases, but I do not propose to go into detail now. The fact that the viscosity acts in this way is rather confirmed by the peculiar action of formate and salycilate ; the sodium formate behaves intermediately as regards the dispersion properties between the organic salts and the inorganic salts, and, as a matter of fact, its viscosity comes in between these two series. Furthermore, sodium benzoate has almost the same surface tension as a normal solution of sodium salycilate, but the sodium salycilate has always greater dispersion capacity than benzoate, but it also has a considerably smaller viscosity. These facts again seem to confirm the possibility that the viscosity plays an important part in these systems.

Since publishing this Paper I have carried out a few more experiments with regard to the solubility, and at the suggestion of Mr. Hatschek I investigated what would be the effect of increasing the viscosity by the addition of such a substance as sugar. I tried that experiment. You know sugar has the effect of increasing viscosity very considerably, and practically it has no effect on surface tension. I have not had very much time to do this work, but I have carried out one series of experiments, namely, on the solubility of leucine in sodium sulphocyanide, and I found that the addition of sugar, even up to 10 per cent., made a very small difference in the solubility. The deviations, in fact, were within the limits of experimental error.

I have just one more series of experiments I should like to show you, somewhat in contrast to the other series. I investigated the action of these various salt solutions on the critical solution temperature of phenol and water —I am showing this, as it is of some interest in that the critical solution

temperature was fairly high, and at higher temperatures the difference between the viscosity of different salt solutions tends to diminish. Now, in this series of experiments, the critical solution temperature of phenol in water alone is 66·7; the critical solution temperature of phenol and tenth normal sodium sulphocyanide is 68·2, the sulphocyanide solution having a slightly greater surface tension than water. In this series, where the differences between the viscosities tend to diminish, you find that the critical solution temperature follows very closely the surface tensions. The viscosities in this case have very little effect—or, rather, the viscosities measured at ordinary atmospheric temperature.

I will not venture to speculate on the part played by viscosity in those systems; I will simply content myself with having put before you a few of my chief experimental data.

Dr. W. Ramsden (Oxford): A brief account of some experiments which Mr. N. G. Chavasse and I have made on the viscosities of "denaturated" egg-albumin solutions may be of interest in this discussion. We have prepared series of protein sols in which the sols, although of the same concentration and not improbably identical chemically, differ greatly in various physical properties, these differences being due, probably entirely, to differences in the size of the "solution aggregates."

The method of preparation adopted is based on the observation made by one of us that egg-albumin readily undergoes "denaturation"* in strong solutions of urea, and that strong albumin solutions are converted into a clear tough gel of *coagulated* protein, while weaker ones yield *soluble* metaproteins. It appeared possible, therefore, that by denaturating egg-albumin at suitably graded concentrations we should obtain a series of soluble metaproteins graded as to the size of the aggregates formed, and therefore differing from one another much as the graded arsenic trisulphide sols prepared by Schulze and by Linder and Picton, and that comparison of the properties of such a series would throw some useful light on hydrophil colloid sols in general.

We have used both crystalline egg-albumin (containing small quantities of ammonium sulphate) and filtered native white of egg, without any difference in the character of the results obtained. Equal volumes of the albumin solution (sometimes previously acidified) are added to four aqueous solutions of urea of different volumes and concentrations so calculated that the resulting mixture contains an equal concentration of urea (about 50 per cent.), and different concentrations of albumin (ranging from 2 to 3 per cent.). The solutions are then left for a few days at 35° C. (or they may be heated to 100° so as to effect instant denaturation) until control experiments show that the albumin must be completely denaturated. The three stronger sols are then made up to the same volume and concentration as the weakest sol by addition of suitable quantities of water and urea (mixed when the denaturation mixtures were made up and kept under the same conditions) and in this way a strictly comparable series of four sols obtained.

The advantages of using urea are: (1) denaturation occurs at low temperatures and without addition of acid or alkali or evidence of breaking off of any constituent of the protein molecule; (2) bacterial action is entirely prevented; (3) no "neutralization precipitate" occurs when acid or alkali is added (unless the urea be too much diluted); (4) the denaturated

* By "denaturation" is understood modification of the albumin into a protein (metaprotein) which is insoluble in pure water or in half-saturated ammonium sulphate solution, but is still, under appropriate conditions, heat-coagulable, and is soluble in dilute alkalies or acids.

protein obtained exhibits great stability as regards the physical characters of its sols.

Although the precise rôle of the urea is at present obscure, we think this obscurity is, for our immediate purpose, unimportant. Since the urea was present in enormous molecular proportions relative to the albumin (*e.g.* 50,000 : 1), any differences in the protein products would be determined by differences in the concentration either of the albumin or of the electrolytes of the albumin solution or of electrolytes resulting from changes in the urea rather than by differences in the mass-influence of urea itself. We find experimentally, however, that the effects of differences in the concentration of electrolytes present during denaturation are quite negligible, as regards the physical properties of the product, in comparison with the overwhelming effects of slight differences in the concentration of the albumin. On these grounds we are disposed to believe that between the large gel of coagulated protein and the variously graded metaproteins the essential differences lie in the mere sizes of the aggregates formed, and that if there be any differences which can legitimately be termed chemical, they are of the same nature as the differences between the sols and the irreversible gels of silicic acid. It would appear that the aggregates of metaprotein formed are, *cæteris paribus*, larger the greater the concentration of the albumin at the time of denaturation, and that, once denaturation is complete, they obstinately retain their characteristic *relative* differences of dimensions notwithstanding subsequent dilution and many other changes of environment.

Comparing the sols of any one series we have invariably found very striking differences in physical properties, provided the initial albumin sols had not been too dilute. We found that the greater had been the concentration of protein during denaturation the greater was (1) the opalescence (in acid or acidified sols), (2) the viscosity, (3) the effect of alkali or acid in increasing or decreasing the viscosity and in decreasing or increasing the opalescence, (4) the rate of sedimentation, when from an alkaline sol the protein is precipitated by dilution, followed by feeble acidification or addition of calcium chloride solution, (5) the amount of acid required to redissolve the precipitated protein, and (6) the less calcium chloride is necessary to produce any precipitate. And we have found that no matter how long the sols (if approximately neutral) be kept, or even if they be boiled, the above contrasts persist, and frequently become still more marked. It is even possible to precipitate the protein, and to find that the sols obtained by redissolving them exhibit the original contrasts. The character of these contrasts appears to us to compel the conclusion that the sols of greater initial concentration possess and obstinately retain the larger "aggregates." The effects of acid and alkali upon the viscosity indicate that the aggregates of the dispersed phase consist of small hydrogels which, without any loss of individuality, shrink when acid in small quantities is added to an alkaline sol and swell again when the original alkalinity is restored, just as do large masses of the gel obtainable from strong egg-albumin.

Time does not permit further consideration of all the physical contrasts described, but as regards viscosity, we may point out that the fact that the sols of any one series (containing the same total *volume* of dispersed phase ?) are more viscous the coarser their "grading" indicates that the size of the "aggregates," as well as the relative total volumes of dispersed and external phases, is an important factor in determining the viscosity of hydrophil colloid sols.

Mr. C. F. Cross wished to emphasize a striking point in the communication of the last speaker, the individual persistence of colloidal systems and the correlative influence of their previous (chemical) history as deter-

mining viscosities in the condition of sols. This is a characteristic of all celluloses and derivatives, independent of dispersive media in which examined, hence a constitutional characteristic in the chemical sense.

(*Further Communication received April* 30, 1913.) The recent symposium of our brethren of physical science on "Colloids and their Viscosity" leaves the general impression on the mind of the chemist that, for the present, the general is calculated to be less fruitful than the particular in advancing our knowledge of the colloidal state.

I should like to suggest a complementary symposium on the particular theme of the "Carbohydrates and the Colloidal State," with special regard to the following results of investigations, and problems arising out of recorded researches, and defined thereby:

1. *Continuous reaction* in typical colloids, especially cellulose. Is this an average, *i.e.*, the integral expression of reactions of discrete units (molecular), or is there a complex unit of multi-molecular *dimensions*, but reacting as a solution aggregate?

2. *Interpenetration of Colloidal Systems.*—The lignocelluloses (and other tissue colloids) are compounds of cellulose and a complex of widely divergent constitution, *in quantitatively uniform ratio*, and with reciprocal modification of reactivity but without ascertainable "chemical" bonds of union: is this adsorption of matter-combination by ultimate units?

3. The *time factor* of constitutional change in colloids under reaction, in its bearing on the general thesis that the chemistry of molecular systems, *i.e.*, our systematic "organic" chemistry, is a chemistry of limiting cases and conditions.

4. Cellulose in presence of water conducts the electric current and undergoes polar rearrangements which persist. The bearing of these phenomena on the general thesis that cellulose, as a typical colloid, is constitutionally modified by solution contact with any electrolyte.

5. If the series, dextrose-dextrins—starch-hemicelluloses—cellulose, represent phases of evolution of the colloidal prototype, are the accompanying changes of one form of matter to another accounted for by the more evident facts of anhydride formation, with polymerization by oxygen linking, or are we justified in assuming fundamental changes of configuration, and a more "organic" union of the unit groups, as, *e.g.*, by carbon bonds?

6. The esters of cellulose furnish cycles of profound modifications by combination and decomposition (reversion to cellulose) throughout which the colloidal characteristics of the cellulose are maintained. Further, these cycles involve exposure to extreme conditions of anhydridization and hydration throughout which the anhydride characteristics of cellulose are generally maintained.

What are the bearings of these phenomena on the alternative views suggested under 5?

Dr. P. Schidrowitz: I have not the privilege of being a member of this Society, and I should like to express on that account my thanks to the Council for giving us the opportunity of coming here to-day and taking part in this colloidal feast, for I think it has been little less than that to those of us who have taken in the past, and will take in the future, some interest in this particular branch of chemistry. Unfortunately, I am personally only able to devote a limited amount of time to this subject, and only to a particular corner of it, namely, to the relationship between the viscosity of a certain substance—rubber—and the properties of that material. I was particularly struck by the Papers of Dr. Ostwald and Mr. Hatschek in this connection. Regarding the relationship between the viscosity of rubber solutions and the

physical properties of the rubber itself, I thoroughly agree with Dr. Ostwald's view that this question is by no means as uninteresting and unimportant as it may perhaps appear to some rubber experts. As one of the first to attempt to apply viscosity measurements to rubber problems, I may perhaps be permitted to make some remarks in this connection. It has been suggested that there are so many variables besides those applying to ordinary suspensoid systems, namely concentration, temperature, and degree of dispersity, as to make the problem an almost hopeless one, but with this view I cannot agree either from a theoretical or from a practical point of view. Dr. Ostwald has summarized these variables in a masterly manner, and an analysis of these variables appears to me to indicate that so far as the valuation of quality of a rubber is concerned many of them are not disturbing elements. While we may not be able to say whether a low viscosity is due to the initial properties of the material, to previous thermal treatment, to previous mechanical treatment, or to time, these factors are, except in specific investigations, of no immediate or direct importance to the problem at issue. With regard to solvate formation, this property of the emulsoid colloids is a factor which it appears to me might be taken advantage of, particularly if we bear in mind the important views set out in this connection in Mr. Hatschek's paper. It has indeed now become a practical question as to whether, considering the practical bearing of viscosity determinations, we should not regard the question of solvate formation as perhaps more important than that of the determination of viscosity from a fixed point or points above the commencement of the (approximately) linear part of the curve. So far as I can interpret Mr. Hatschek's communication in this regard, it would appear that there is some parallelism between the variable physical properties of rubber, more particularly of strength, and the concentration at which a rapid rise of viscosity takes place. Looked at from another point of view this amounts to the determination of the concentration at which the disperse system occupies not less than 50 per cent. of the whole volume of the system. We have here again an apparent confirmation of Dr. Ostwald's views as to the importance of kinetic as opposed to static methods.

You may perhaps care to hear very briefly my experience of the practical value of viscosity measurements in connection with the strength and technical value of rubber. These views, I may say, are based on many hundreds of viscosity determinations over the last six years, and in very many cases these determinations have gone hand in hand with the valuation of quality by vulcanization methods. Broadly speaking, one may say that a low viscosity indicates inferior strength, a high viscosity, on the other hand, suggests the probability of strength above the average. Nevertheless, while this relationship holds good in probably the majority of cases, we cannot yet state that it holds good in all cases. If commercial rubber consisted of the pure rubber hydrocarbon as such, the relationship would, in my opinion, undoubtedly apply as a general rule. Commercial rubbers, however, all contain small quantities of impurities, and these impurities may exercise an influence in either direction. It also does not follow that there is necessarily a parallelism between the effect of these impurities on viscosity on the one hand and on the vulcanization process on the other hand. It is for this reason that viscosity estimations in connection with the valuation of rubber must be applied with some discrimination and caution. This remark, I may say, applies to any other method, including that of vulcanization. The latter, indeed, if properly carried out, is and probably will remain the final test in any case, but it must be remembered that if vulcanization tests are to

be carried out so as to have any real value, expensive and heavy apparatus and machinery—in fact, as I know to my cost, something like a miniature rubber factory—is required. Even then testing by vulcanization is not so simple a matter as many, including a goodly number of manufacturers, appear to think. In carrying out viscosity estimations we must bear in mind the fact that we are estimating, or trying to estimate, the viscosity of the main rubber substance and not of the latter plus all the impurities which are contained. So far as my general experience goes, there is a very marked parallelism, with relatively few exceptions, between the viscosity of a given rubber and its quality as shown by vulcanization; as a general statement one may say that as a rapid "sorting out" test for comparing the value of rubbers of the same grade, viscosity determinations have already proved their value. With the improvements in technique and general methods which have been indicated in the Papers read to-day, the application of viscosity methods should be still more valuable in the future than they have been in the past. I think that Dr. Ostwald's suggestion that the viscosity of such a material as rubber, or gelatine, or protein, if subjected to an investigation—to a very complete investigation—would afford extremely valuable data and would lead us into paths of which at present we may dimly see the openings, but certainly not the endings; and I make the suggestion with all respect to those members of this Society, and others, who have the time at their disposal, that an investigation of this kind would not only be of the highest theoretical importance, but also of very great technical value.

Mr. W. P. Dreaper: The influence of the viscosity of solutions of cellulose is a factor which cannot be disregarded in, say, the manufacture of artificial silk. Some of the processes could hardly be worked if attention was not given to this important point. In this respect the apparatus due to Couette as now modified by Hatschek seemed to offer certain advantages.

There is one remark to make about the communication made by Dr. Ramsden, and that was to suggest that possibly the aggregates mentioned do not consist of metaproteins but of adsorption compounds formed by the urea and the albumin, similar to what one probably got in a solution of gelatin which contained gallic acid in quantities insufficient to cause actual coagulation. One might expect such aggregates to be stable under the conditions mentioned in Dr. Ramsden's Paper. From work he had undertaken with Mr. J. G. Davis in connection with the adsorption of colloidal solutions of dye-stuffs by a column of sand, he thought that important results might be obtained by this method in determining the solution state of colloids from the point of view under discussion.

Dr. James W. McBain (Bristol) spoke on the "Mobility of Highly-charged Micelles."

It has been a great privilege to be present at so eminent a gathering of distinguished visitors, and I should like to add my congratulations to the Council of the Faraday Society.

I should like to say a word or two arising out of Professor Pauli's very suggestive Paper.

Professor Pauli has mentioned a difficulty which results from a comparison of the viscosity of acid- and alkali-albumins, as measured mechanically, with the unexpectedly high mobility of these same viscous ions when measured by means of electrical conductivity. This behaviour is not peculiar to albumins; it is one of the outstanding problems in much simpler systems, such as soap solutions. . Thus a concentrated solution of a sodium stearate is a thick gum, but it exhibits a conductivity only somewhat less than that of sodium acetate.

In other words, this discrepancy is a general phenomenon with such colloidal electrolytes.

There is another difficulty which Professor Pauli has not mentioned, nor indeed have I seen it pointed out anywhere. We are finding that Stokes's law, which governs the friction of small particles moving through a liquid, may be applied more and more extensively. It has even been applied with more or less success to molecular disperse systems. This law states that the work required to move a constant amount of disperse substance through a liquid is directly proportional to the degree of dispersion. Even if this law may not hold quantitatively it may yet be taken as a qualitative guide for our present purpose. Now take some of these highly charged colloidal aggregates, micelles or "colloidal ions" we are discussing. On account of the law of electroneutrality we must assume these high charges to correspond with the number of free ions of opposite charge (as Professor Pauli has done in his Paper). But if, say, a dozen electrons, instead of each being busy moving its own tiny molecular disperse ion, may all club together by uniting their burdens, they will by this manœuvre have only a tithe of their former work to do, and the result will be a very fast ion—one of very high mobility. Now experiments so far show that this is not the case; the most mobile micelle has only a mobility comparable with that of a rather slow true ion. Here is the second discrepancy then: these micelles having ten times the electrical force to do the usual work and yet producing only the ordinary ionic mobility.

I think that the meeting will now anticipate what I am about to say, when I point out that these two discrepancies go to meet each other: the discrepancy mentioned by Professor Pauli—abnormal mechanical viscosity and yet ordinary electrical mobility; the second discrepancy—abnormally high mobility predicted and yet only ordinary mobility found. In accordance with Professor Pauli's own views outlined in his address and also in accordance with certain remarks of our Chairman, we have to assume excessive hydration of these very highly charged micelles (possibly as a consequence of their electrical charges). This would account for their abnormally high mechanical viscosity and at the same time for their mobility being only normal.

This would seem at first sight a very happy issue out of the difficulty emphasized by Professor Pauli, but I am really very loth to urge this explanation, partly because I foresee some difficulties in the way of applying it to the case of soap solutions without making very daring further assumptions, and partly because I have not yet had an opportunity of working it out in detail.

Arising out of this I must mention a problem which is now being met in the investigation of soap solutions and similar systems. I refer to the comparison between the conductivity and the osmotic properties (boiling-point, etc.). A normal solution of sodium palmitate has a conductivity almost comparable with that of sodium acetate, yet its rise of boiling-point is only a quarter as great as that of the sodium acetate and the conductivity cannot be due to the presence of hydroxyl ions, for (unpublished) quantitative measurements have proven that the concentration of these is only a few thousandths normal. These unpublished measurements were carried out by Cumming's dew-point method. Congo red, as studied by Donnan and Bayliss, is very similar, for one has to assume complete dissociation to account for the conductivity, and yet its osmotic pressure as measured directly corresponds to an undissociated solution of a non-electrolyte. In the case of the soaps, on account of the dew-point method being employed,

the true osmotic pressure is obtained, and the criticisms with regard to pseudo-osmotic effects which may be urged against the direct determinations do not here apply. This contradiction between the results of conductivity and of osmotic pressure would seem to be one of the most important colloidal problems awaiting definite solution. The suggestion I made above would be in the right direction here also, but I do not yet care to state that it would be a perfectly satisfactory explanation for soap solutions, which are the systems with which I am the most familiar.

Professor T. Turner (Birmingham) : May I venture to direct attention to viscosity of a class of material that has not been mentioned to-night ?—I refer to metals. The viscosity of a number of metals above their melting-point has been determined by Professor Fawsitt and found to be not very much greater than that of water. Of course, as the metals cool and solidify the viscosity increases, and ultimately we get a micro-structure of metals or alloys, or of any single-phase solution, which we well recognize, on solidifying, as being exactly like that given in (*a*) of Mr. Hatschek's Paper (p. 84). In that case the continuous phase is the portion which has solidified last, and the discontinuous one is the portion which has solidified first. Now, in rolling a metal, we are dealing with a viscous substance and we have a deformation, and apparently the second diagram (*b*) is the typical structure of a rolled metal. It is a curious fact that when you first roll a metal and it becomes harder, as a rule the density is increased ; but if you continue rolling the metal and it becomes still harder the density is then again decreased.

I notice it is stated that, " If shearing is continued, the system has of course a tendency to assume its original shape"—tending to go back again to these polygonal areas in section. If it is so, we have no microscopic evidence to support that view ; but it is very likely with magnifications greater than we employ at present you might be able to obtain definite evidence. At all events, the facts as to density to which I have referred tend rather to support the view. I would venture to suggest that the microscopic examination of materials which have a viscous character would afford interesting information as to the nature of the changes which take place during deformations due to pressure.

Mr. F. P. Worley : From the point of view of one who has not made a special study of this subject it seems remarkable that no attention has been paid in the discussion to the effect of the colloid or dispersed substance on the water itself. It is universally admitted that water, the only solvent considered, is not a simple substance, but is a highly complex mixture of different aggregates of the simple H_2O molecules in equilibrium. This being the case, it is to be expected that any substance dissolved or dispersed in the water will disturb the equilibrium and will in general tend to increase the proportion of the simpler constituents. Substances such as butyl and amyl alcohols which have little tendency to combine with water have a very important influence on processes occurring in aqueous solution, as for instance on the solubility of salts and on the rates of various chemical interactions. The influence of such substances is due in all probability to the changes they produce in the water itself. In the case of substances which become considerably hydrated on being dissolved, such as salts and sugars, such effects may be marked or counterbalanced by other effects, but it is probable that all substances present in water in a highly dispersed condition tend to simplify the water complexes. In the case of colloids the effect on the water will probably depend on the degree of subdivision, but we can be tolerably certain that the water will always be affected to a greater or less

degree. As any change in the water is likely to have an important effect on the viscosity, it is imperative that consideration of this point should not be neglected.

Dr. C. J. Martin, after expressing his great indebtedness to the authors of the Papers and to the Faraday Society for affording him the privilege of being present at the meeting, hoped that in their reply the authors would further indicate what interpretation they thought might be placed upon a rise in viscosity in a colloidal system occurring under particular conditions. Mr. Hatschek had with great ingenuity arrived at a satisfying explanation of the high viscosity and the variations of viscosity with concentration of oil-water emulsions in which the dispersed phase exceeded 70 per cent. His formula also held good in the case of strong casein solutions in which the protein particles certainly imbibed water and were much greater than the volume of the protein itself. The agreement, however, seemed to occur too soon, viz., when by the calculation the dispersed phase was only 50 per cent. of the total volume and the particles were not necessarily in contact. He suggested that the fact that the particles of protein in a sodium caseinogenate solution were charged would in itself contribute to the rigidity of the system, as this would limit the degree of freedom of movement as soon as the emulsion became at all concentrated. By this means deformation of the dispersed particles might be a necessary accompaniment of shear long before the volume of the dispersed phase had reached the proportion when the particles composing it were in actual contact.

This effect of charge might also explain in part the increase in viscosity of "ionized" protein discovered by Professor Pauli.

Dr. Martin pleaded guilty to a further "superstition," that, within a certain order of magnitude, the size of the particles had itself an influence on viscosity, and would much like to hear Professor Henri's views as to this possibility.

Mr. W. R. Bousfield, M.A., K.C., *communicated* a "Note on the Theory of Viscosity."

In a paper published in 1906 * I set forth a theory of viscosities which should, I think, be considered in relation to the viscosity of colloids, though I have had no opportunity of applying it to this subject.

If $r_1, r_2, r_3 \ldots$ be the average radii of the various molecular varieties in a liquid, $m_1, m_2, m_3 \ldots$ the proportions of each, and $C_1, C_2, C_3 \ldots$ constants for each variety, the viscosity of the heterogeneous mixture could be expressed as

$$\eta = \Sigma Cmr/\Sigma m.$$

This was shown to be true for certain mixtures and to account simply for various phenomena—such as "negative viscosity"—which had been the subject of a good deal of speculation.

The application of this theory to colloids would appear to promise useful results.

Professor H. N. Morse [Johns Hopkins University] (*communicated*): Although you propose to limit the discussion to the *viscosity* of *colloids*, I should be tempted, if present at the meeting, to inject, if opportunity offered, the question whether *semipermeability* is not an attribute of colloids *only*. If it is (and probably most of us would give an affirmative answer), are our colloidalists giving a due amount of attention to this wonderful characteristic? Our very particular interest in this question is due to the fact that, during

* "Ionic Size in Relation to the Physical Properties of Aqueous Solutions," *Phil. Trans.*, A, vol. 206, pp. 129–42.

our twelve years' experience with osmotic membranes, we have learned that their continued efficiency depends entirely upon the maintenance of the colloidal state.

Professor Victor Henri said that Mr. Hatschek had assumed a cellular structure for emulsoids, in which the walls were formed by the continuous phase. He himself had observed the reverse structure, viz., a cellular or reticulated one, in which the walls or the network were formed by aggregates of the *disperse* phase, while the spaces contained therein were filled by the continuous or liquid phase.

As regarded the constant in the Einstein-Hatschek formula, he thought that the various methods of measuring the sizes of ultra-microscopic particles were not sufficiently exact to base on them criticisms of the formula.

Professor H. Freundlich : I should like to point out a number of things which have been brought to my mind, especially by the words of Dr. Martin. It is not quite untrue when he says that we do not actually know what viscosity measurements really mean. As long as we use viscosity alone for comparative experiments—for comparing different qualities and different sols—it is of the greatest value. I hardly need mention that after the Papers of Professor Pauli and others. You know how easily we can detect very slight changes in solutions by measuring viscosity.

But this is somewhat different if we want to know what any viscosity measurements mean. You must remember that we do not know anything about the viscosity of normal solutions—I mean, we do not know any theoretical relation between the viscosity and the concentration of a common solution of molecular disperse substances. We do not know any theoretical relation between the viscosity and the concentration even of the simplest solution—let me say a solution of urea, or of sugar ; and there is no wonder that we do not know anything about the systems which are decidedly more complex, as the colloid solutions are.

Now the Paper of Mr. Hatschek shows that we have perhaps the simplest case if we look at solutions which contain a small amount of a disperse phase, the particles of which we can consider as absolutely rigid, and showing no interaction, or, at least, the smallest possible interaction, with the solvent itself. We know that we here have to deal with a formula somewhat of this kind—

$$\eta = \eta_0 (1 + K\phi).$$

This formula seems to be one of the few really consistent things we have, because it follows out of the theoretical deductions of Einstein and of Hatschek, and really does agree in small concentrations in a number of cases. It agrees for very dilute silver sols ; it agrees for gamboge, and also for very dilute suspensions in the experiments of Bingham and Durham *—although I do not believe them to be of great value, the suspensions being so concentrated—nevertheless it does agree in the smaller concentrations ; it agrees in those experiments I have lectured about to-day, for they do not refer to anything else but to changes in the viscosity of suspensions of $Al(OH)_3$. But this agreement does not go so far as to include the numerical value of the factor K. It is strange also that the values calculated from a theoretical standpoint vary. Einstein first calculated $K = 1$; Hatschek calculated 4·5 ; then later Einstein calculated a value of 2·5. And the measurements themselves give very different values, values which vary even on a much larger scale. I should like to ask Mr. Hatschek if he has formed an idea as to what causes these large variations ?

* *Amer. Chem. Journ.*, 46, 278 (1911).

The Chairman : We have no cases of purely spherical particles ; you can only get spherical particles in exceptional cases.

Professor Freundlich : Do you not think that the particles of gamboge are spherical ? I should imagine them spherical myself.

The Chairman : Yes, but the surface need not be smooth.

Professor Freundlich : That may be so. But I believe what is still more important is that we have very few cases absolutely of that kind, that there is no interaction between the particles and the solvent——

The Chairman : The trouble is we know the weight but not the volume.

Professor Freundlich : But have you not formed certain ideas about the numerical value of K? What causes a larger value for K, what causes a smaller value ? This question seems to me important, because I believe this formula to be to some degree fundamental, it being in any case the first formula of this kind having a theoretical foundation.

The Chairman : If I may interpose at this stage, we agree as to the importance of the formula, but spherical particles—which are the only ones capable of mathematical treatment—with a smooth surface and without an adsorption layer are almost impossible of realization. We get very near them in the starch suspensions tried by Wm. Harrison, who found a numerical coefficient of 4·75 with all starches. I propose to repeat his experiments, but with starch suspended in carbon tetrachloride, which does not cause it to swell. A great variety of shapes is possible and more probable than a spherical one. To take an extreme case, gold can be obtained in very thin hexagonal plates by appropriate methods of reduction, and it is quite conceivable that such plates may occur in metallic or other sols. If a liquid containing such particles were sheared, the plates would arrange themselves probably parallel with the planes of shear, and the coefficient would come out very much smaller than 4·5. In other cases the particles might be polyhedra, say, for instance, rhombohedra. Such a body might arrange itself in different ways towards the direction of shear, and the coefficient of friction would not only be different from that of a sphere, but would be different with different orientations. Only regular polyhedra might possibly (as in the theoretical case of motion in a perfect fluid) behave like spheres. So you see that there is a very considerable range of variation possible, but I think such variations in the numerical constant do not in any way detract from the value of the formula. I think all this will probably make Dr. Martin more doubtful than ever about the value of viscosity measurements, but that cannot be helped.

Professor Freundlich : I only want to add a second remark, in order to emphasize something which Mr. Hatschek has said : it is that we must take into regard the method with which we measure the viscosity. As long as we only make comparative experiments, there is nothing to be said against the use of a simple viscometer, *e.g.*, of the Ostwald type, but as soon as we really want to know anything theoretical about the viscosity of colloidal solutions, we decidedly ought to use different methods, or at least a method where we are absolutely sure of the velocity of the shearing and so on. And I should like to point out that it perhaps would be of value to make those viscosity experiments which Sorkau * made with pure liquids — he varied the velocity to such a degree that he got a turbulent flow and a superturbulent flow—also with colloidal solutions and see how they behave then. Sorkau has succeeded in finding the foundations of a comparatively simple theory in regard to pure liquids, and it might not be impossible that experi-

* *Phys. Zeitschr.*, 12, 582 (1911) ; 13, 805 (1912).

ments with colloidal solutions, or better with suspensions, might elucidate the theory of their viscosity in a marked degree.

The Chairman: At present I have confined myself to defining the limits beyond which turbulent flow begins in my apparatus, and have kept below them. That is the first thing to do.

Professor Freundlich: Decidedly.

Dr. Wo. Ostwald (*partly communicated April* 28, 1913): With regard to Professor Freundlich's question as to the causes of the variation in the values of K in the viscosity formula, a question the importance of which I should also like to emphasize, I may be permitted the following remarks. Apart from any roughness of the surface or from any asymmetry of the disperse particles, a variation in the size of the adsorption envelope seems to me in the first place to be responsible for the variation of the experimentally determined values of K. The Chairman has already emphasized that as a rule we know the *weight* instead of the *volume* of disperse phase—and, I would add, the weight of non-solvated or non-hydrated disperse phase. To this must be added that doubtless the size of this adsorbed or adhering layer, which owing to the Brownian movement must already produce, as it were, a "kinetic" increase in the volume of disperse phase, varies with the special nature of disperse phase and of dispersion medium. Even in typically suspensoid sols such a variation must appear, *e.g.*, according to whether we have glass or metal as disperse phase. I remind you of the old experiments with so-called adhesion plates, which, according to their chemical composition, lifted different quantities of liquid. It also seems probable to me that the size or else the effect of these adhesion or adsorption layers varies with the concentration of the dispersoid. One may certainly imagine the case that, with medium or higher concentrations, the dispersion medium may be held simultaneously by several disperse particles, so that the surface is "unsaturated" as regards adsorption. This would cause a considerable solidification, *i.e.*, an increase in viscosity, etc.

As regards Dr. Martin's "superstition" that the degree of dispersity, notwithstanding the theoretical verdict, influences the viscosity, I must confess that I entirely share it. Apart from all the experimental evidence of this fact, and also of the correction which, according to Mr. Hatschek, results from variation in the adsorbed volume with varying degree of dispersity, I can quote at least one case in which such a dependence can also be deduced theoretically. This is the case of typical emulsoids. Mr. Hatschek has shown in one of the first of his brilliant series of papers on these subjects that the deformability of a drop of liquid depends greatly on its size. He has shown—and in his customary manner illustrated by several neat figures and calculations—that the "rigidity" of such a drop increases fairly rapidly and distinctly with increasing dispersity, a fact which, for instance, enables us to separate fine oil emulsions, like suspensoids, by a filter. If such a drop can be deformed by motion, as in a viscometer, its surface grows with constant volume, *i.e.*, its specific surface, and this in any case means an increase in friction. It follows that there is a range of dispersity in emulsoids, in which viscosity must decrease with growing degree of dispersity.

I may be allowed to close my remarks with the following. Dr. Martin has, among other suggestive remarks, put the question: What do all these viscosity measurements mean, what do they really show? Dr. Martin has failed to find an answer, and Professor Freundlich in his previous remarks has endorsed this view. I must confess that I cannot see what else we have been doing all this time if not to show what viscosity measurements mean.

Is not this perhaps an apparent problem, a mere rhetorical question, somewhat like the sentence often met with : "We know so much about electricity, but we still do not know what it really is." At the bottom of this query there is often the want of a theory, as molecular or kinetic as possible, which shall explain all these phenomena deductively. If Dr. Martin with his question meant to express the desire for a comprehensive theory of the phenomena of viscosity, I can of course only agree with him from my fullest conviction. Only I hold the view, on one hand, that a large number of contributions to such a theory exist already (A. Einstein, E. Hatschek, etc.), so that the "nature" of viscosity is no longer in need of, as it were, "sudden illumination"; and, on the other hand, I think that the phenomenological part of our knowledge of viscosity is no less important for its "nature" than the mathematical theory applied to ideal cases. I can therefore not quite agree with Professor Freundlich that, because we "have no theoretical relation whatever between concentration and viscosity in molecular disperse systems" we therefore "know nothing at all about the viscosity of ordinary solutions." This seems to me somewhat too strong an emphasis on the theoretical side of the question. I only make this remark because this view suggests a slight, if certainly unintentional, depreciation of the numerous and valuable investigations of those authors who up to now have worked more on the phenomenological aspect of viscosity and who have thereby, *inter alia*, prepared the ground for a complete theory of viscosity. I hold that these inductive experimental investigations are no less important for elucidating the "nature" of these phenomena than the mathematical theory, and that the identification of "nature" and "theory" in the above sense is not justified. "Once a fact is known from *every* side it is thereby explained, and the task of science is finished," says J. R. Mayer. To all these "sides" the inductive and experimental knowledge of the phenomena belongs no less than their deductive mathematical theory.

The Chairman : I have only a few remarks to make in reply to various points raised in the discussion. Professor Henri has sketched an alternative structure, in which the solid or more viscous phase forms the network, *i.e.*, the reverse of the structure assumed by me in an emulsoid. Such a structure, however, is really a gel structure, with which I do not profess to deal, having, in fact, in several papers emphasized the impossibility of doing so. I understand that Professor Henri's observations were made between slide and coverglass, and I must confess to a great distrust of such observations, as the mobility of the phases is too much impeded.

Dr. Martin's remarks have been dealt with by Dr. Ostwald. As regards Dr. Ramsden's results, I will only refer to the statement that his various sols contained the same volume of albumin. All that is certainly known is the weight, and the question whether equal weights always mean equal volumes is at the bottom of most of the difficulties of the subject.

We have also been advised to consider the effect of the association of water on the viscosity of aqueous sols. It has been a misfortune of colloidal chemistry that so much work has been done, perhaps necessarily, with water as dispersion medium. I think it is very desirable that phenomena should be studied which are as free as possible from complicating factors, in the present instance sols in organic solvents, etc.

Before calling on Dr. Senter to propose the vote of thanks to those who have contributed to the discussion, I will ask Mr. Chaston Chapman to show us some of his interesting colloidal solutions.

Mr. Chaston Chapman said that the solutions to which the Chairman

had referred had been prepared in the course of an investigation of which he proposed to give a full account to the Chemical Society, and consequently he would content himself with showing the solutions to the members and describing them very briefly. The orange-coloured solution was a solution containing in the colloidal condition a little stannous oxide and a considerable quantity of an oxide of tin intermediate between stannous and stannic oxide —in all probability the sesquioxide. The solution had been prepared from stannous tartrate and had been dialysed for a considerable time so as to free it entirely from the excess of tartaric acid. It could be evaporated nearly to dryness without becoming insoluble, but if it were completely dried then it could not again be dissolved in water. On heating for some time in the presence of air, the coloured solution became colourless, owing to the formation of stannic oxide in the colloidal condition. On adding sulphuretted hydrogen to the orange-coloured solution a deep brown solution resulted, containing in the colloidal state sulphide of tin corresponding with the intermediate oxide.

These solutions were shown by Mr. Chapman, who in conclusion demonstrated to the meeting the coagulation produced by the addition of a drop of hydrochloric acid.

Dr. G. Senter: Before the meeting disperses I have the pleasant duty of proposing a very hearty vote of thanks to all the authors of Papers and contributors to the discussion. This motion could not, of course, be put from the chair for obvious reasons, as Mr. Hatschek has been one of the most important contributors to our proceedings. I am sure you will agree with me that we have had a very enjoyable and instructive meeting. This successful result is due in no small measure to the contributions of Professors Freundlich, Henri, and Pauli, and of Dr. Ostwald, who have come from abroad at great trouble to take part in the discussion. I ask you to indicate by your applause our great obligations to our foreign colleagues for their presence and contributions, and also our thanks to Mr. Hatschek and the other speakers, who, although they may not have come from so great a distance, have also greatly contributed to the success to our proceedings.

The proposition was carried with acclamation, and the meeting then terminated.

THE CORROSION OF IRON AND STEEL.

At a meeting of the Faraday Society held at the Manchester School of Technology on Friday, April 4, 1913, conjointly with the Manchester Section of the Society of Chemical Industry, a GENERAL DISCUSSION on "THE CORROSION OF IRON AND STEEL" took place. Dr. Gilbert J. Fowler was in the Chair.

AN ELECTROLYTIC THEORY OF THE CORROSION OF IRON.

BY BERTRAM LAMBERT, M.A.

(*A Contribution to a* GENERAL DISCUSSION *on* "THE CORROSION OF IRON AND STEEL," *held before a Joint Meeting of the Faraday Society and the Society of Chemical Industry at the Manchester School of Technology, Friday, April* 4, 1913.)

The application of electrolytic ideas to the question of the corrosion of iron has been discussed by Whitney,* Cushman,† Tilden,‡ Walker,§ Armstrong,‖ and many others, but much confusion and misunderstanding has arisen owing to the different interpretations used by the various writers.

The American writers have discussed the question from the standpoint of Nernst's conception of the source of electromotive force between a metal and a solution. It seems to follow from their reasoning that all iron (even if it be chemically pure and physically homogeneous) ought (*a*) to rust in contact with air (or oxygen), (*b*) to cause the deposition of copper from solutions of copper salts.

The present writer's experiments ¶ have proved beyond any doubt that iron can be prepared which will not rust on long exposure to air and water (either distilled or ordinary tap-water), and will not cause the deposition of copper when placed in even strong solutions of copper sulphate or copper nitrate under ordinary conditions.

It also seems to be thought by many supporters and opponents of electrolytic theories of corrosion that any electrolytic theory of the corrosion of iron must "stand or fall" on the question of the solubility of iron in pure air-free water.

* *Journ. Amer. Chem. Soc.*, 1903, **25**, 394.
† *Trans. Amer. Elektrochem. Soc.*, 1907, **12**, 403.
‡ *Trans. Chem. Soc.*, 1908, **93**, 1356.
§ *Journ. Iron and Steel Inst.*, 1909, **1**, 70.
‖ *Science Progress*, 1911, **22**, 311.
¶ *Trans. Chem. Soc.*, 1912, **101**, 2068 *et seq.*

The object of this Paper is to show that a simple and natural development of the ideas of Faraday on electrolysis will give us the foundation of a satisfactory theory of the corrosion of iron—a theory incomplete as yet owing to the lack of experimental facts, but one which is quite in accordance with well-established facts and which is not affected by the question whether iron is soluble to any appreciable extent in pure air-free water.

It is well known that whilst ordinary commercial impure zinc readily dissolves when placed in dilute sulphuric acid, the pure metal is scarcely affected unless metallic connection is made between it and another more electronegative metal, either within or without the liquid. Under these conditions the pure zinc dissolves, but the action ceases immediately the metallic contact between the pure zinc and the more electronegative element is broken.

In impure zinc the more electronegative element is already present within the mass of the metal, in the form of minute impurities, such as copper or lead, or perhaps as another form of the metal which is relatively electronegative to the main mass of the metal.

Whenever we have two metals (or two modifications of the same metal) which are electrically different, that is, have different solution pressures, and they are placed in metallic contact in an electrolyte, then the relatively electropositive part will dissolve with the production of an electric current flowing through the electrolyte from the electropositive to the electronegative pole, and in the opposite direction through the metal.

The rate of such a reaction depends: (*a*) on the magnitude of the difference of electric potential—that is, the difference of solution-pressure between the two metals or the two modifications of the same metal, and (*b*) on the resistance offered by the electrolyte to the passage of the electric current.

No part of the metal can dissolve unless an electric current actually passes through the electrolyte. The rate of the reaction may, however, be so infinitesimal that the amount of metal passing into solution will not be sufficient to respond to chemical tests even after long periods.

Let us consider, in this light, the case of a piece of ordinary commercial iron in contact with the electrolyte water.

Such a piece of iron is impure and not homogeneous—there are some parts of it which have a different solution-pressure from other parts, and so, when it is placed in contact with the electrolyte water, we have all the conditions for the production of an electric current.

If the conditions are such that an appreciable electric current can pass between the two electrically different parts of the iron, the metal will dissolve at the relatively electropositive parts. The fact that iron is practically insoluble in pure water (in the absence of oxygen) shows that the current which actually does pass is so infinitesimal that the amount of iron dissolved cannot be detected, even after long periods, by chemical means.

This may be due to two causes, namely, (*a*) the small magnitude of the electromotive force owing to the small differences of potential between the electrically different parts of the metal, and (*b*) the great resistance offered to the passage of an electric current by the electrolyte.

The writer's experiments* seem to be generally accepted as proving beyond any doubt that commercial forms of iron will undergo corrosion quite readily in contact with pure water and pure oxygen in the complete absence of carbonic acid or any other acid—that the only essentials for the corrosion of ordinary iron are water and oxygen. It is generally believed that iron must pass

* *Loc. cit.*, pp. 2056 *et seq.*

through a process of solution before rust is produced, and so, whilst the metal is practically insoluble in pure water alone, it must be soluble in the presence of oxygen. It follows, then, that oxygen must bring about some alteration in the conditions of the "voltaic circle"—commercial iron and water—in such a way that a greatly increased electric current passes between the electrically different parts of the iron. That oxygen can bring about such a change of conditions is beautifully illustrated by an experiment described by Dunstan and Hill.* Cushman † has shown that if a piece of commercial iron is left in contact with a solution of sodium chloride to which a little phenolphthalein has been added, a pink colour develops in the solution which is in contact with some parts of the metal. These colour zones, which are always confined to a portion (or portions) only of the metal, indicate the presence of hydroxyl ions (or free alkali) at these points. After being kept some time, the metal beneath the pink zones remains quite bright, but corrosion takes place gradually at the other parts of the metallic surface. This experiment shows that the solution is being electrolyzed, and that the iron is passing into solution at those parts not marked out by the pink colour of the phenolphthalein. It shows also that some parts of the iron are electrically different from other parts, and that the electromotive force produced by these differences of solution-pressure is enough, under these conditions, to cause the passage of an electric current of sufficient magnitude to produce perceptible electrolysis of the solution of sodium chloride.

It was shown by Dunstan and Hill, however, that the extent of this electrolysis was conditioned by the presence of oxygen, because, in the absence of air (or oxygen) the pink zones were not developed, and therefore an electric current sufficient to produce perceptible electrolysis could not pass.

Oxygen, therefore, must do one of two things—it must in some way or other increase the electrical differences between the parts of the metal and so increase the electromotive force, or it must reduce the resistance of the circuit. When a piece of commercial iron is put into water in a vacuum, iron strives to pass into solution at the relatively electropositive part of the metallic surface, but hydrogen, produced by the electrolysis of the water, is deposited at the relatively electronegative part. This film of hydrogen, forming almost instantaneously and covering up the negative pole, introduces an enormous resistance into the circuit, and reduces the electric current to an almost negligible strength, so that the rate at which the iron passes into solution is infinitely small.

Oxygen dissolved in the water probably acts by oxidizing the hydrogen thus deposited at the negative pole—destroying the polarization—and so allowing a greater current to pass between the electrically different parts of the metal.

If this argument is true, then commercial iron ought to pass into solution, *in the absence of oxygen*, if it is placed in an electrolyte, such as copper sulphate solution, where, instead of the non-conducting hydrogen film, there would be a conducting film of metallic copper produced at the relatively electronegative pole. Experiment shows this to be true. Commercial iron, when brought into contact with a solution of pure copper sulphate in a vacuum, causes the immediate deposition of copper on the iron just as readily as when the experiment is conducted in the presence of air; in a short time all the copper is removed from the solution and iron takes its place.

It seems to be clear then that when commercial iron rusts in contact with

* *Trans. Chem. Soc.*, 1911, 99, 1853.
† Amer. Soc. Testing Materials, 1907.

air and water, oxygen plays an important part in the actual dissolving of the iron, quite separate and distinct from its later function of converting the dissolved iron into rust.

The formation of rust from the dissolved iron is not, as is sometimes supposed, a simple oxidation of the ferrous ions. It is not possible for the ferrous ion to be oxidized to the ferric ion by means of ordinary molecular oxygen. This can readily be proved by a simple experiment. If a solution of ferrous sulphate is made strongly acid with sulphuric acid and oxygen is passed through the solution, comparatively little ferric salt will be found in the solution even after the oxygen has been passed through it for several days. The greater the proportion of free sulphuric acid present, the less the oxidation which takes place. The oxygen only oxidizes the undissociated ferrous hydroxide formed by the hydrolysis of the ferrous salt, and since ferrous hydroxide is a very weak base, hydrolysis is very considerable unless a large excess of acid is present.

In the rusting of iron, then, the metal passes into solution as ferrous ions owing to electrolytic action between the electrically different parts of the iron, oxygen playing an essential part in the process. The ferrous ions then combine with the hydroxyl ions present in the water to form undissociated ferrous hydroxide :—

$$Fe^{\cdot\cdot} + 2OH' = Fe(OH)_2.$$

At this stage oxygen plays a second part, converting the ferrous hydroxide into ferric hydroxide or some hydrated form of ferric oxide (rust).

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3.$$

The fact that iron rust produced under ordinary atmospheric conditions is shown, on analysis, to contain carbonic acid—that rust formed under such conditions is a basic carbonate of iron—does not necessarily prove, as has been supposed, that carbonic acid plays any essential part in its formation. Wet ferric hydroxide absorbs carbon dioxide, so that the carbonic acid found in rust formed under these circumstances may very probably have been absorbed from the air by the rust after its formation.

It follows from the theory that if we could produce metallic iron chemically and physically homogeneous it ought not to rust, because there would not be any differences of solution-pressure on its surface, and therefore no cause for the production of electric currents when the iron was placed in an electrolyte.

It would follow also from the theory that the production of a coherent and absolutely homogeneous coating, of whatever nature, on the surface of commercial iron would prevent corrosion. The bearing of this on the question of passivity is discussed later.

The Properties of Chemically Pure Iron considered in connection with the Electrolytic Theory of Corrosion.

The present writer * has prepared chemically pure iron, and it has been found that such iron can be exposed to the action of air (or oxygen) and water (either distilled or tap-water) for an apparently indefinite time without showing any signs of corrosion. It must be strongly emphasized, however, that *chemical* purity is not the only essential.

In the preparation of pure iron by the writer's method the same sample

* *Trans. Chem. Soc.*, 1910, **97**, 2430 ; 1912, **101**, 2068.

of ferric nitrate, treated in exactly the same manner throughout its conversion into iron, will not always give like specimens of the metal.

One batch of iron will rust quite readily, whilst another batch can be exposed for many months to the action of air and water without showing any signs of corrosion. All the pieces of the same batch behave, as a rule, in a precisely similar manner. Now any difference between the batches cannot be due to differences in *chemical* composition. The only possibly variable factors are temperature of reduction and rate of cooling, and so differences in the product must be of a *physical* and not of a chemical character.

It is a very striking fact that the pieces of iron which will not rust can also be put in solutions of copper sulphate or copper nitrate, of any strength, without causing copper to be deposited on the iron, while pieces from a batch of iron which rusts always cause the deposition of copper from the same solutions of copper salts. Sometimes the copper is deposited quickly, whilst at other times several hours may elapse before the deposition of copper takes place. The metal is always attacked at one or more points, and the deposition of copper spreads from these points over the whole surface in a very short time.

It is clear from these experiments that physical differences in iron of the same high state of chemical purity can cause most profound differences in its behaviour.

If the theory is true, we should expect such results. In the case of the iron which does not rust and is unaffected by solutions of copper sulphate or copper nitrate, the metal is probably physically homogeneous,* at any rate on the surface. There would, therefore, be no differences of solution-pressure—no electrically different parts—on the surface of the metal, and so no tendency for the metal to pass into solution by electrolytic action when the metal was put into an electrolyte. Since iron could not, therefore, pass into solution, we should not expect rusting to take place, nor should we expect the deposition of copper on the iron from solutions of copper salts.

The processes preceding corrosion and the deposition of copper from copper-salt solutions upon metallic iron are undoubtedly similar in character.

In the case of the samples of pure iron which rust and which cause the deposition of copper from solutions of copper salts, the metal, although chemically pure, is not physically homogeneous, owing probably to some inequality in the temperature of reduction or the rate of cooling.

If such be the case, differences of solution-pressure would exist on the surface of the metal, and when it was put into an electrolyte there would be a tendency for electric currents to be set up between the electrically different points. In water, in the presence of air, this would lead to corrosion, in copper-salt solutions to the deposition of copper. An interesting confirmation of such an argument is furnished by the following experiments.

Some pieces of the pure metal were taken which had been exposed to the action of water and air for several months without showing any signs of corrosion. They were carefully dried between pure Swedish filter paper, and then some of them were subjected to pressure in a polished agate mortar by an agate pestle, while others were left untouched. Some of the pressed pieces were then put in distilled water and exposed to the air; they rusted in the course of a few hours, rust forming first at the edges which had not been pressed by actual contact with the agate, whilst the pressed portions

* It is not necessary to assume absolute homogeneity. The electrical differences on the surface must, however, be so minute that the rate at which the iron is passing into solution is infinitely small.

remained quite bright. Others of the pressed pieces were put into a solution of copper sulphate ; copper was deposited immediately on the metal, deposition first commencing at the unpressed edges of the pieces.

The pieces of iron which had been dried but not pressed neither rusted when placed in contact with water and air again, nor did they cause copper to be deposited from copper sulphate solution, so that it was the application of pressure alone which caused the profound alteration in the properties of the iron.

This again is readily explained by the theory. If a piece of iron be originally homogeneous and part of it be subjected to a strain, then the piece will consist of two parts, a strained and an unstrained part—it will contain two different modifications of iron, each having a different solution-pressure. If such a piece of iron be put in an electrolyte, there would now be a tendency for the passage of an electric current between the two electrically different parts, and so we should expect corrosion to take place when the iron was placed in contact with water and air. The fact that corrosion and the deposition of copper begin at the unpressed part shows that this part is relatively electropositive to the pressed part.

These same points are illustrated in a striking and very beautiful manner by the use of the ferroxyl reagent described by Cushman and Gardner.* The pure iron which does not rust is unaffected by the ferroxyl reagent, whilst the pure iron which is not physically homogeneous, or has been subjected to pressure, causes the development of the beautiful colours which indicate electrical differences, or differences of solution-pressure, on the surface of the metal.

There are, however, some properties of pure iron which could not be predicted from the theory, but which cannot be considered as arguments against it.

The behaviour of pure iron towards solutions of copper chloride is altogether different from its behaviour towards solutions of the sulphate and the nitrate. Pure iron which has remained uncorroded after many months in contact with water and air, or which has remained unaltered in solutions of any strength of the sulphate or nitrate of copper, causes the immediate deposition of copper when placed in a solution of copper chloride, even when the solution is very dilute. The same effect is produced if sodium chloride is added to copper sulphate or nitrate solutions in which the iron has remained unaffected for long periods. The experiment is very striking if carried out in the absence of air. The iron quickly disappears, leaving behind finely divided copper, which in the course of a few hours is itself converted into white insoluble cuprous chloride.

Further, if a tube be taken containing pure iron which has remained unaltered in copper-sulphate solution for a long period, and the temperature of the tube be raised to 100° C., copper is deposited on the iron, and in a short time all the iron passes into solution, leaving behind small crystals of copper.

These facts led the writer to suspect that the pure iron might conceivably be covered with a thin coherent film of some protective substance, and most careful experiments were carried out to test this possibility. It was finally decided, as the result of these experiments (*loc. cit.*), that this curious behaviour could not be accounted for by the presence of a protective film of either oxide or hydride on the iron.

The curious behaviour of the pure iron towards copper-chloride solutions

* *Corrosion and Preservation of Iron and Steel* (1910), p. 48.

is interesting if considered in connection with the behaviour of the metal in sodium-chloride solution. Even very dilute solutions of the chlorides of the alkali metals have a remarkable action in starting the corrosion of pure iron which has withstood the action of water and air for long periods without showing any signs of corrosion. The action of salt solutions on pure iron is at present under investigation, and the results are not ready for publication.

It is well known that ordinary commercial iron is rendered passive by certain substances, *e.g.*, nitric acid, solutions of caustic alkalies or chromic acid, and that such passive iron, so long as the passivity persists, will not rust in contact with pure water and pure oxygen, and will not cause the deposition of copper from very dilute solutions of copper sulphate.

In view of what has been said above, it seems probable that these substances have the power, in some way or other, of altering the surface of commercial iron so as to destroy, temporarily, the electrical differences on its surface—to produce what might be described as an "electrically equable" surface. The result of this would be that the iron would possess no tendency to go into solution in an electrolyte and so would not rust when placed in contact with air and water.

Much the same sort of "electrically equable" surface is produced in a plate of impure zinc when it is amalgamated.

Since passivity can be produced by such widely different substances, it is not improbable that the "electrically equable" surface produced is not always of the same nature.

The writer is inclined to the view, which is as yet unsupported by experimental evidence, that substances which protect iron from corrosion have the power, in some way or other, of destroying or reducing the electrical differences which always exist in commercial forms of iron—that they have a passiviving effect—and that the substances, like the chlorides of the alkali metals, which stimulate corrosion do so by increasing these electrical differences. This would explain the remarkable behaviour of pure iron towards copper-chloride and alkali-chloride solutions. For the present, however, the subject must be left open.

ELECTROLYTIC METHODS FOR PREVENTING CORROSION.

By Professor W. W. HALDANE GEE, B.Sc., M.Sc.Tech.

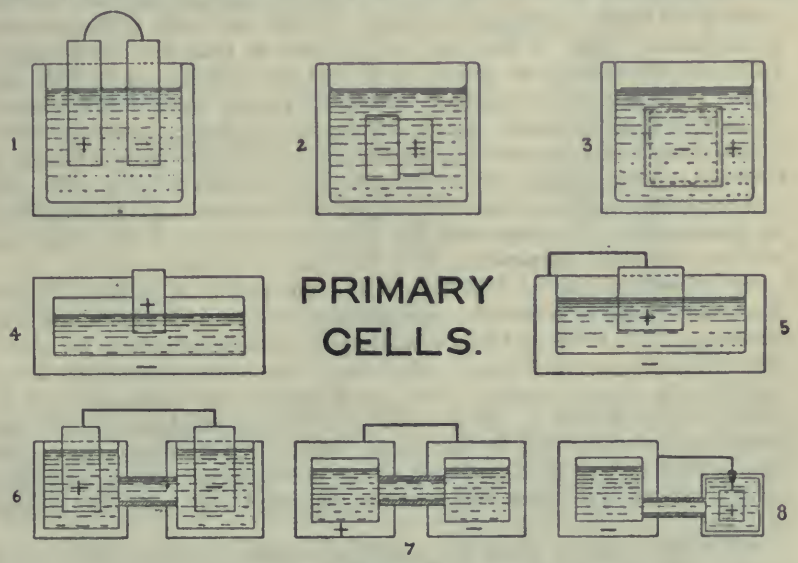
(*Abstract of a Lecture delivered before the Joint Meeting of the Faraday Society and the Society of Chemical Industry at the Manchester School of Technology, Friday, April* 4, 1913.)

The corrosion of metals may be lessened or prevented in two ways :

1. By connecting the metal to be protected to a more electropositive metal so that a primary cell is produced.
2. By making the metal to be protected the cathode in an electrolytic cell supplied by an external electrical pressure.

Primary Cell Method.

The arrangement of the parts of the primary cell may be as shown in Figs. 1–8, where the metal to be protected is marked — and the protecting



Figs. 1–8.

metal by +. In Figs. 1–5 both electrodes are immersed in the same vessel, but in Figs. 6–8 a separate anode and cathode vessel is used, so that the products of electrolysis may be kept to a certain extent separate ; the vessels are supposed to be connected by insulating tubes and externally by wires. In Figs. 1 and 5 external connections are also used, but in the case of Figs. 2, 3,

and 4 the electrodes are in short circuit, Fig. 3 illustrating the case where the protecting material forms a more or less perfect coat on the metal to be protected. Other varieties of the primary cell method might be included, but the above show the chief cases that occur in practice.

In all the cases the lines of flow shown in the diagrams will be complicated.

The current strength C in these simple cells will be given by the general formula:

$$C = \frac{E - e}{B + R + x'}$$

where E is the pressure of the cell, e is the total polarization pressure, B the internal and R the external resistance, whilst x denotes the resistance of any contacts or that due to any films, etc., that may be produced at the electrodes.

The analysis of the primary cell method especially demands the consideration of the effective voltage. It depends on the potential difference of each metal in the electrolyte, the polarization effect at the anode and cathode, and when hydrogen is liberated at the cathode an extra voltage, called *overvoltage* or the *Caspari effect*, necessary to liberate the gas is required. Unless hydrogen can be easily liberated and removed at the cathode, the overvoltage may have an important value. Metals show great differences in the ease with which they allow this discharge. In 1833 Bouchardet* made experiments by placing zinc balls in various metal vessels with an electrolyte of dilute sulphuric or hydrochloric acid and ammonium chloride, and determined the loss of zinc in a certain time. Assuming that the zinc balls were similarly placed in each case in equal-sized vessels and that the resistance of the short-circuited primary cell was the same for each electrolyte, then the order of the effective voltages will follow directly the order of the amounts of corrosion. Thus in the case of Zn-brass in HCl, the overvoltage is small and the strength of current large, and the corrosion of the zinc also large. The greater the strength of current the greater the protective value of the cathode from corrosion; hence zinc should be a good protector of brass. On the other hand, zinc would be a poor protector for tin, the overvoltage of tin being especially high. Since the importance of overvoltage in promoting and preventing corrosion has been realized, much attention has been given to its measurement. It varies with the physical condition of the metal and with the time and temperature, also with current density.

Sir Humphry Davy's "Protectors."—The prevention of corrosion by the direct application of a more to a less positive material, as in Fig. 2, was suggested by Sir H. Davy, and his attempts by this means to prevent the corrosion of the copper sheathing of ships due to the action of sea-water are of considerable historic interest. They are detailed in the *Transactions* of the Royal Society for 1823–5. He found that a relatively small area of the more electropositive metal iron or zinc would protect copper from corrosion, but the method had to be abandoned owing to the clean copper forming a surface on which shell-fish and seaweed flourished and made the bottoms very foul.

Since the work of Davy very many experiments have been made which confirm the protective action of zinc on iron, and an extensive literature could be quoted. There are many patents in which the same principle is embodied. Among the experiments the work of D. Phillips may be quoted. He carried out experiments for eight years, and the results of his experiments with both hot and cold liquids are detailed in the *Proc. Inst. C.E.*, 85, 295, 1886.

* Tommasi, *Traité de l'Electrochimie*, p. 198; *J. Pharm.*, 1833, p. 457.

Professor Ernst Cohen of Amsterdam read in 1902 a paper on "The Corrosion of Condenser Tubes and Sea-Water Conductors" before the Institution of Naval Architects. He was attracted by the experiments of Davy, and showed that marine engineers might use Davy's method with advantage. He arranged the following experiments :—

1 (see Fig. 9). A and B are glass cylinders connected by a U-shaped glass tube C. A, B, and C are filled with sea-water. In A is a piece of copper or brass, and in B a very small piece of iron or zinc. The metals are connected by a wire. He found that the metal in A remains bright, whilst that in B dissolves. By altering the length of C the influence of the resistance of the water in the connecting tube can be tested.

2 (see Fig. 10). This is a similar experiment, but air can be drawn

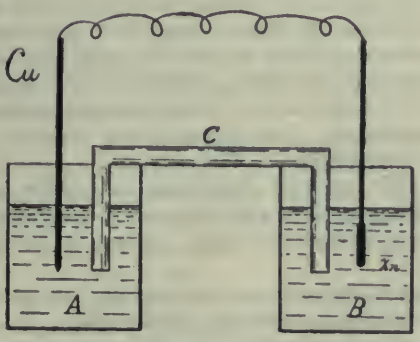


FIG. 9.

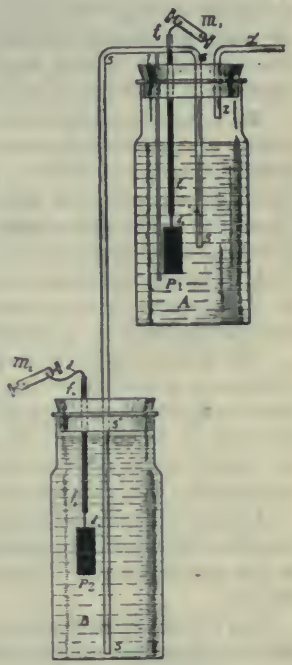


FIG. 10.

through the tube *l* into A by connecting Z' with an air-pump. The copper P_1 in A then corrodes ; but if the zinc P_2 in the lower vessel B be connected (with the aid of the clamps m_1 and m_2) by a wire to the copper in the upper vessel, the corrosion of the copper ceases. By varying the length of SS the length of the tube that gives a resistance too great to be effective in preventing corrosion can be found. Here the copper or brass plate corresponds to the condenser tubes on board a ship, P_2 to a piece of zinc suspended in the sea, and S with the tube connecting the condenser with the sea.

In 1898 Diegel confirmed the result of Davy that both zinc and iron would act as protectors of copper and brass. More recently Engineer Rear-Admiral Corner * has detailed cases where the presence of iron strongly

* *Journ. Inst. Metals*, 1911.

counteracts the corrosion of copper and brass. Zinc is not found so efficient a protector as iron, for the reason that with the latter a better metallic contact can be maintained.

In the Harris-Anderson Patent System and Apparatus for the Protection of Condenser Tubes from Corrosion Pitting (the Harris Patent Feed-Water Filter (1910), Ltd.), a protector of aluminium or an alloy of this metal is used. The patents are Nos. 355 (1905) and 8393 (1905). Aluminium, or an alloy of this metal, is claimed as superior to zinc, for when zinc is employed it is necessary to remove the zinc from time to time in order that its surface may be cleaned. Instead of placing the protector in a separate outside vessel as described in Patent No. 8393, it is the more usual practice of Harris and Anderson to place the protector inside the water-end of the condenser. Wires connect the alloy to the tube-plate. It is essential that the tubes themselves be in proper metallic contact with the tube-plate. This is secured, in the case of screwed ferrules, by the use of compressible metallic washers. The protective blocks may be carried on studs, the exact arrangement depending on the type of condenser.

In using aluminium and some of its alloys, some precautions must be taken. Essentially it is a very positive metal. In normal solutions its tabulated potential difference is about ½ volt above that of zinc. But it will be found on testing the potential difference between Al and Zn in NaCl solution that Zn is the more positive metal, and that in a galvanic couple of the two zinc is the metal to be corroded. At about 70° C. the potential difference changes sign. This is explained by the action of the hot salt solution on Al. The Al is attacked by hot and moderately strong solution of NaCl and the electronegative film is dissolved. The film, on cooling the liquid, reforms.

Use of Zinc in Boilers.—The protection of steam boilers from corrosion introduces a new phase of the problem. Here we have to deal with an electrolyte which may reach with high-pressure steam a temperature of from 150–200° C. It will hence be of the first importance to know the conductivity of boiler waters up to such temperatures. The determination of water-conductivity has become of interest to engineers in other ways.*

Again, at such temperatures the potential difference of metals in the electrolyte and the effective voltage will be very different to the value at low temperatures. There is need of research work relating to these matters.

The introduction of zinc in boilers has been in use for about eighty years, and there has been much discussion amongst engineers as to its utility. It is evident that zinc will act as a neutralizer of acid waters, but would in this respect be more expensive and less efficient than the use of an alkali. With certain waters it will certainly help to prevent incrustation of the boiler.

Lumps of zinc placed in boilers can only effect local electrical protection. A complete zinc sheathing has been proposed by R. Bell.† Merely placing the zinc in trays, hangers or stirrups will not ensure metallic contact, and the action of the zinc to prevent corrosion under these circumstances will be weak. The experience of W. C. Ward is that if zinc is used in sufficient quantity, and properly applied and connected to the boiler, the protection afforded is *perfect.*‡

It is advised to use 1 square foot of zinc for 50 square feet of boiler surface at first, and then diminish to 1 square foot to 100 feet. It is stated

* See "The Digby-Biggs Conductivity Tube," *Trans. Farad. Soc.*, Vol. VI., p. 167, 1911.

† *Trans. Inst. Naval Arch.*, 1869, 10, 174.

‡ *Cassier's Magazine*, 7, 490, 1895.

that H.M.S. *Crocodile* has used 425–630 lb. of rolled zinc per boiler per annum.* J. Morris † mentions a case where slabs of 12 inches by 12 inches by 1½ inches disappeared in six weeks.

If the amount be 400 lb. per annum, this will correspond to about 17 amperes if the zinc is used in accordance with Faraday's law.

Where there are brass fittings in the boiler, local corrosion of the iron may be induced. Here the presence of the zinc may be of considerable importance in altering the distribution of the electrical stream lines so as to tend to protect both the iron and the brass from corrosion. ‡

The difficulty of attaching the zinc to the iron support may be overcome, it is suggested by Hambuechen, § by the following method :—

The iron rod is coated with tin, which would be detrimental to the boiler if it were not for its overvoltage. From this tinned rod iron plates of zinc may be suspended by means of a tinned stirrup. The exposed tin, acting as a cathode, will be kept clean and therefore always give a good electrical contact. A convenient form for the zinc will be as rings coated on the inner surface with tin, which can be slipped over the tinned iron rod.

Use of External Electrical Pressure.

That the electrical current required for protection could be supplied from an external galvanic battery probably occurred to Sir H. Davy, ‖ but, like many other early suggested applications of electrical energy, was not economically possible, on account of the expense of the maintenance of primary cells. Now that the supply of cheap electrical energy is so general, the use of an external pressure for protection against corrosion deserves the careful attention of chemists and engineers. The first consideration will be the current density necessary for adequate protection. The following experiments made at the Manchester School of Technology show that quite a low value is sufficient :—

I. Two plates of transformer iron were used. Total area of each plate 102 square cm. They were placed for 38 hours in a 5 per cent. salt solution. The average loss was 0·57 per cent. They were then made the anode and cathode in the same strength of salt solution with a current density of about 0·66 amperes per square cm. The cathode gained 6·4 per cent., the anode loss was 70 per cent.

II. Plates of good sheet iron were pickled for 20 hours in a 1 per cent. hydrochloric acid solution, when the black scale was loosened. This was scrubbed off and the plates were made quite clean. They were then placed in a 1 per cent. sodium-chloride solution for 166 hours, which produced an average loss of 0·78 grams. They were then cleansed and immersed for 168 hours in a new solution of 1 per cent. salt solution. The average loss was 1·38 grams. After again cleaning, the plates were made the anode and cathode in 1 per cent. salt solution, and a current was passed for 42 hours ; a copper voltameter in the circuit gave an average current of 0·105 amperes. The anode loss was 6·6 grams, whilst the cathode gained 0·12 gram. The loss due to self-corrosion should be 0·35 gram ; the calculated corrosion produced by the current is 5·15 grams. This experiment shows that a current density of

* See C. E. Stromeyer, *Marine Boiler Management*, p. 84, 1907.

† *Naval Arch.*, **23**, p. 151, 1882.

‡ See F. S. Spiers on some experiments on voltaic cells with compound electrodes, *Electrical Review*, vol. 45, p. 911 and p. 953, 1899.

§ Carl Hambuechen, *Trans. Am. Electrochem. Soc.*, **18**, p. 44, 1910.

‖ See the *Life of Sir H. Davy*, by Dr. Paris, vol. ii., chaps. xiii and xiv, 1831.

0·000097 amperes per square cm., or 0·088 per square foot, is more than sufficient to protect the iron against the corrosion of the salt solution.

III. Six electrolytic cells were arranged in series with electrodes and vessels of the same size. The electrolyte in three of the vessels was stirred by rotary stirrers worked by a motor. A current density of 0·24 amperes per square foot was used for 10 hours. The vessels that were stirred were at once distinguished from the others owing to the production of brown ferric compounds, whilst only green corrosion compounds were formed in the vessels in which the contents were at rest, excepting at the surface in contact with the air. The electrolytes were Manchester tap water, 1 per cent. sodium chloride, and 1 per cent. hydrochloric acid. The cathodes in the two former cases showed a small gain, but with the acid there was a small loss. The loss with the 1 per cent. acid was when stirred 0·0243, and not stirred 0·012 gram per square foot per hour.

IV. Separate anode and cathode vessels were used, and a slow current of 1 per cent. salt solution was made to flow from the cathode to the anode vessel, so that the anode product was prevented from entering the cathode vessel. With a current density of 0·15, the cathode showed a small loss.

V. Electrolytic cells were made up with plates of clean ferrotype iron. In each cell there were three plates placed parallel to each other about 2 inches apart. The central plate was made the cathode, the outer plates were anodes, so that the current density on each side of the cathode was about the same value. The following mean results were obtained :—

Current Density. Amperes per sq. ft.	Gain or Loss per sq. ft. per hour of Cathode in grams.	Electrolyte.
0·0268	+ 0·000698	Manchester tap water.
0·0067	— 0·00103	1 per cent. NaCl solution.
No current	— 0·00672	„ „ „

VI. Like the previous experiment, but with copper (electrolytic) electrodes :—

Current Density. Amperes per sq. ft.	Gain per sq. ft. per hour of Cathode in grams.	Electrolyte.
0·014	+ ·00059	3 per cent. NaCl solution.

These results should be compared with the experiments of G. Harker and J. Macnamara.* They found that the anode loss was approximately, in the case of iron and steel in ordinary and sea water, in accordance with Faraday's law, and they suggested that it might be possible to find the current required for protection by calculating it from the loss by ordinary corrosion. This in the case of iron in sea-water was equivalent to about 0·004 ampere per square foot. When this current density was used, the iron was found to be protected.

A paper presented at a joint session of Section XA of the Eighth International Congress of Applied Chemistry, held in New York City, by J. K. Clement and L. V. Walker has just been made available by its publication

* *Journal Soc. Chem. Industry*, p. 1286, 1910.

in the *Transactions* of the American Electrochemical Society, vol. xxii., p. 193. It describes the continuance of the experiments commenced by F. M. Stanton relating to the prevention of the corrosion of steel immersed in acid water by the electrical method. They used solutions of sulphuric acid from N/5 to N/1,000, and found that the current density necessary to prevent the corrosion of steel plates depended on (*a*) the rate of stirring of the electrolyte; (*b*) the amount of oxygen present; and (*c*) the acid concentration. Of these factors (in the case of dilute solutions) the rate of stirring is the most important. Although they employed carbon anodes, they found that the minimum current density required could fairly well be calculated from the loss by corrosion without current, as in the case of Harker and Macnamara's experiments. The latter had concluded that the electrolytic process does not actually prevent metal from entering the solution from the cathode,

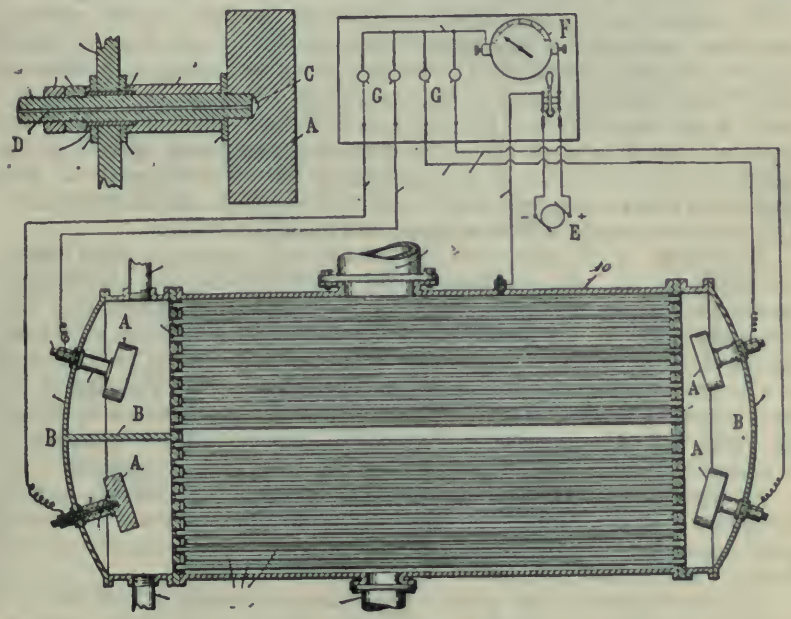


FIG. 11.

but this loss may be compensated by the plating-out of the iron. With a carbon anode this explanation (if no iron is in solution) fails, and the protective action of the current must be attributed to the prevention of the formation of ferrous ions by the action of the liberated hydrogen. If oxygen or other depolarizer is present, the minimum current density will be greater owing to the removal of the hydrogen. The more rapidly the liquid is stirred, the greater will be the depolarizing action and the greater the current density needed to effect protection. In the experiments of Clement and Walker a current density of from 0·072 to 0·144 ampere per square foot was found sufficient to prevent corrosion.

Mr. P. Elliott Cumberland has in the British Patents 13417 (1907), 8422 (1908), 8068 (1909), 19637 (1911), and 4251 (1912) elaborated the electrical method for the protection of surface condensers, steam boilers, propeller shafts and stern posts of ships, and other metallic structures. In Patent No. 8422 anodes of carbon are fixed in the boiler by insulated pressure

plugs. In Patent 8068 (1909) the continuity of the electrical supply is ensured by the use of both a dynamo and storage cells, the latter being automatically brought into use when the dynamo is stopped. Regulating resistances are provided and an ammeter is included in the circuit so that the current density can be controlled.

In Fig. 11 are shown the details of Cumberland's method for the prevention of the corrosion of a surface condenser. Here there are four anodes (which are marked A) fitted in the removable end-plates B. The anodes are of iron, the details of their support and insulation being shown in the upper diagram. When they have corroded to the point C, water will flow through the hole D and will act as a "tell-tale" that a new anode must be fixed. The source of electrical pressure is a 110-220 volt dynamo E, connections being made through a switchboard; the latter is provided with an ammeter F, and four metallic filament lamps G, which will act as visible indicators of the current supply to the anodes. Under ordinary conditions—even with a large condenser—one ampere per anode is found to give adequate protection. Cumberland's method applied to a Babcock and Wilcox boiler is shown in Fig. 12. Three anodes G are used in the water space, and one G at the lower end of the tubes. The former are fixed to a bar A, and are connected through the insulated studs F to the switches S, and resistances R to the ammeter on the switchboard C. The shell of the boiler is connected at B to the cathode of the double-pole switch. The electrical supply is from a small, low-voltage generator.

The results of the application of Cumberland's process to many marine and land boilers and condensers have been satisfactory. Lieutenant-Commander Frank Lyon, of the U.S. Navy, from his experiments has concluded that: (1) this process stops corrosion; (2) it removes scale from heating surfaces and prevents the formation of scale; (3) it may be used as a water alarm, for when the electrode is placed with its lower edge at the level indicating that the danger zone for the water and lights are in circuit, the lights fail when the electrode is not in contact with the water; (4) it is economical as far as electrical energy and anodes are concerned.

Amongst a number of other patentees of details for utilizing electric currents are Messrs. Harris and Anderson. They have devoted themselves more especially to the protection of the tubes of surface condensers (see British Patent 18220 (1911)).

They have verified that quite a small current density is sufficient for adequate protection, prolonged experiments giving a *minimum* value of 0·0012 amperes per square foot. In the case of a certain condenser of 1,025 square feet, 2 amperes at 2 volts is continuously supplied. This corresponds to a current density of about 0·002 amperes per square foot, and to an annual expenditure of energy equal to 35 Board of Trade units. They generally use the same anode blocks for "assisted" (that is, without external e.m.f.) as for "unassisted" protection, and it has been found that the loss of the electrode in the former is not very much greater than in the latter case. The actual cost of the special anodes used by Messrs. Harris and Anderson varies from £3 to £5 per 1,000 square feet per annum, according to different circumstances.

The U.S. Patents of H. S. Anderson and J. W. Berrie (796172 and 769390, 1905) apply electric currents for the protection of the metallic screens used in concentrating plant from the corrosive action of acids. A graphitic anode is used. If the concentrated liquid contains sulphuric acid or copper sulphate—as is usual in the treatment of ores containing copper sulphide—either hydrogen or copper will appear on the screen (which is made the

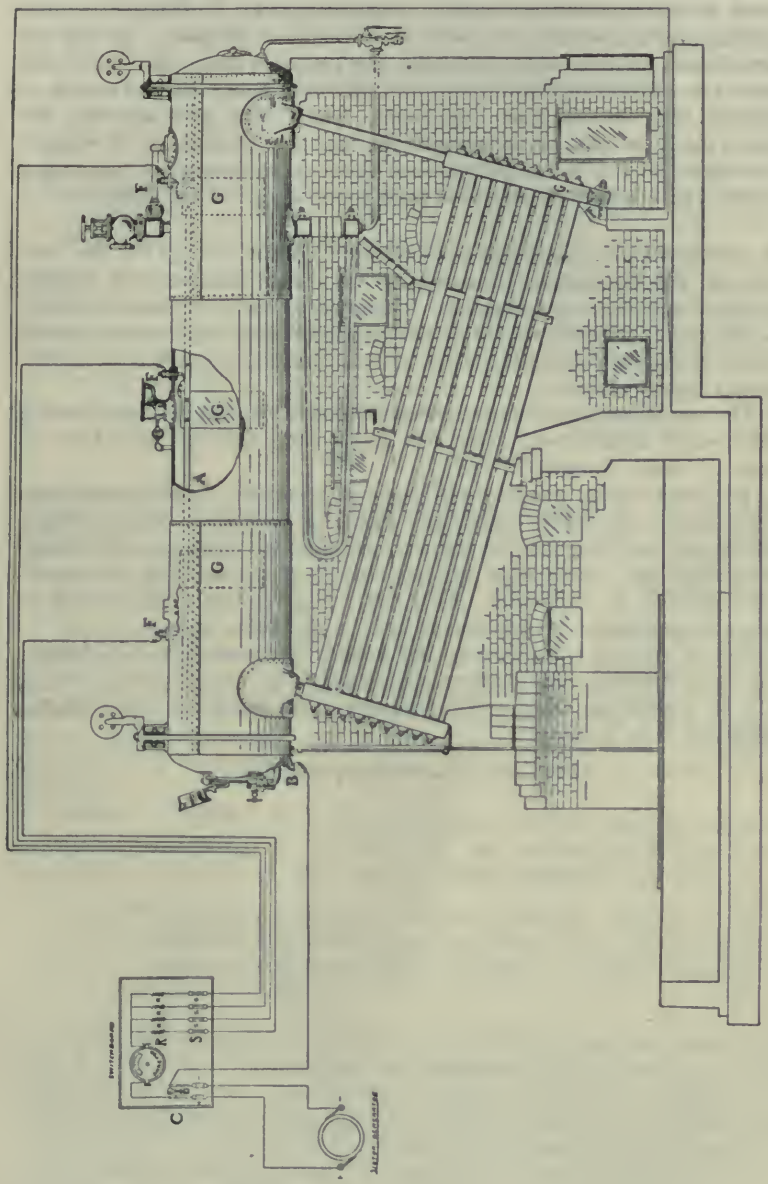


FIG. 12.

cathode), and the corrosion of the screen will be prevented. With the use of electrical currents they find that it is possible to substitute steel wire or punched steel screens for the much more expensive ones of copper or brass.

It has already been stated that with direct currents boiler scale may be removed or its formation prevented. According to E. R. Dolby,* a small alternating-current magneto may be used for the same purpose. By the use of woodite and asbestos iron electrodes are insulated from the boiler and connected to one terminal of the magneto, the other being earthed and so in connection with the shell of the boiler, which was also earthed. He attributes the prevention of the scale to the alternate production of oxygen and hydrogen on the boiler plates, these gases recombining and forming a thin film of pure water, which would hinder the deposit of the scale.

In conclusion, the application of cheap electrical energy for the prevention or the diminution of corrosion in metals deserves the serious attention of engineers and chemists. Commercial success demands that—

1. The current density should be sufficient, and that this current density be equally distributed over the surface to be protected by a sufficient number of anodes rightly placed.

2. The anodes and electrical connections should be well insulated and the insulation well maintained. (This will apply with more especial force in the case of steam boilers.)

3. The nature of the anodes must be rightly selected. In some cases they may be soluble, in other cases they must be insoluble. Where soluble electrodes are used they may be placed in a separate vessel, and precautions taken to avoid the introduction of the products of corrosion at the anodes into the cathode compartment. This will apply especially to the case of solutions in process of concentration in iron and other pans.

I wish to express my thanks to Mr. Elliott Cumberland, and to Messrs. Harris and Anderson for information placed at my disposal; also to Mr. D. M. Fairlie for help with the experimental work. A more detailed investigation is in progress.

* *Proc. Inst. C.E.*, vol. 99, p. 88 (1890).

THE NATURE OF OVERVOLTAGE.

By J. I. CRABTREE, M.Sc., A.I.C.

(*A Contribution to a* General Discussion *on* "The Corrosion of Iron and Steel," *held before a Joint Meeting of the Faraday Society and the Society of Chemical Industry at the Manchester School of Technology, Friday, April* 4, 1913.)

It is well known that the voltage necessary to decompose a dilute acid electrolytically varies with the nature of the electrodes employed, that is, the metals involved possess different decomposition voltages for that acid, which are invariably in excess of that of platinized platinum.

Let E_m and E_p be the decomposition voltages of a given acid with electrodes of a metal m, and platinized platinum respectively.

$$\text{Then } E_m = E_p + \eta.$$

This excess value of the decomposition voltage η, over and above that observed with a platinized platinum electrode, is termed the "überspannung," "sur-tension," or "overvoltage" of that particular electrode.

According as the gas separated occurs at the anode or cathode, we speak of the "anodic" or "cathodic" overvoltage.

The overvoltage of a metal has also been considered from the standpoint of the electromotive force of polarization or back e.m.f. set up at an electrode after being polarized, in so far as different metals polarized by the same gas, *e.g.*, hydrogen, give different values for this back e.m.f. Accordingly, Le Blanc defines overvoltage as the excess of the back e.m.f. set up at the electrode over that given by a platinized platinum plate under identical conditions.

Methods of determining η, the Overvoltage.—Several methods have been proposed. According as the value of the overvoltage is calculated in accordance with one or other of the above definitions, we have :—

1. "Decomposition voltage" methods—η being obtained directly by subtracting the decomposition voltage when using a platinized platinum plate from that given by the metal in question.
2. Back e.m.f. methods.

1. The decomposition voltage may be found by connecting the electrodes with a current supply and observing the point at which continuous electrolysis first sets in when the applied potential is gradually increased. This stage is recognized by noticing the bubble formation, after the method of Caspari,* or as in the method of Müller,† by connecting the circuit through a galvanometer and observing the point of sudden increase of current or "knickpunkt" representing the change from "residual current" to that of continuous electrolysis.

Since the decomposition voltage represents a quantity equal in magnitude to the sum of the single decomposition potentials at each electrode, we

* *Zeitschr. Phys. Chem.*, 30, 89, 1899. † *Zeitschr. anorg. Chem.*, 26, 1, 1900.

can find these individually by the method originally devised by Fuchs.* The metal in course of examination is arranged as cathode, placed with an anode of platinum in a vessel containing dilute sulphuric acid and electrolyzed. By connecting the electrolyte behind the cathode by means of a siphon tube to a normal electrode, the voltage of the complete cell may be obtained, and hence that of the single electrode by simple subtraction.

2. A third method is due to Le Blanc.† The method employed in the present work is a slight modification of this. By means of a double commutator driven by a motor the electrodes of the electrolytic cell were connected for a short interval to a primary circuit, thus causing electrolysis of the solution. This circuit was then broken, and during a second interval, the cathode and a normal electrode making connection with the same electrolyte were connected with a slide wire potentiometer and the e.m.f. thus evaluated.

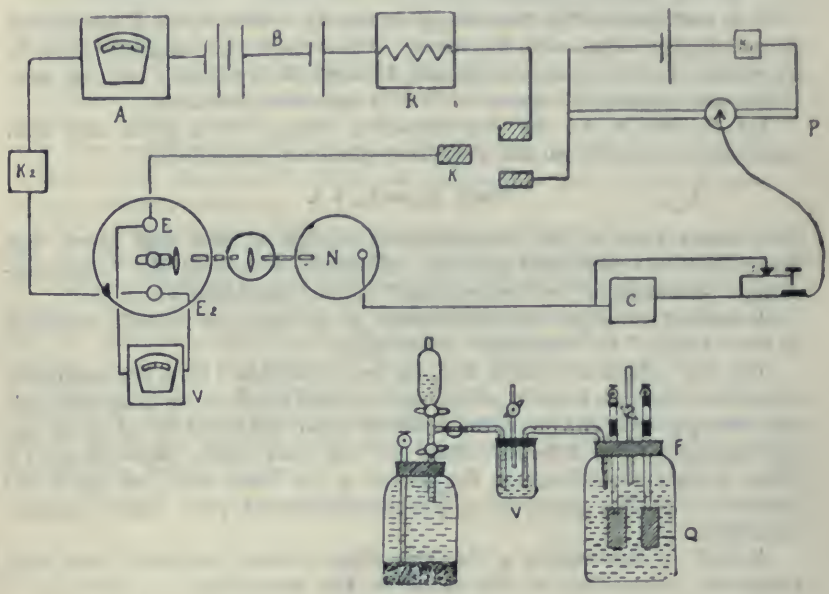


DIAGRAM I.

From this the value of the back e.m.f. of polarization of the electrode was obtained. By means of a rapid rotation of the commutator (20–30 revolutions per second) the effect was essentially equivalent to an independent activity of both primary and polarization current. Also a considerable variation of speed of the commutator made no difference to the value of the potential measured. The apparatus employed is shown in the diagram above.

The primary circuit was connected with a battery of cells B; which were connected to the electrodes E_1 and E_2, an ammeter A, regulating resistance R, and plug K_2 being included in the circuit. By this means a current either of increasing amperage or e.m.f. could be employed for the electrolysis: a voltmeter V being shunted across the terminals of the cell. The commutator K, on breaking the primary circuit, connects the cathode E_1 (say) and the normal electrode N with the potentiometer P, whereby the e.m.f. between

* *Ann. der Physik.*, 156, 1875.
† *Zeitsch. Phys. Chem.*, 5, 469, 1890.

these electrodes is compensated by a known measured e.m.f., a capillary electrometer C being employed as "null" instrument. This was of the Ostwald vertical type, exhausted, with a capillary of elliptical section whereby a maximum sensitivity was obtained. A cathode of platinized platinum was then used at E_1, and the difference between this reading and the former gave the overvoltage direct. The electrolytic cell connected with the normal electrode is shown at F in elevation. It consists of a glass vessel fitted with a rubber stopper, through which pass the electrodes and a glass tube connected with the intermediary vessel V, which serves to facilitate the connecting together of the cell, and also prevents accidental entry of electrolyte from the standard cell into the electrolytic vessel.

The normal electrode used was the Hg/Hg_2SO_4 element, with acid of the same concentration as that used in the electrolytic vessel, whereby boundary potentials were eliminated, and likewise all possible source of contamination of the electrolyte in K by potassium chloride, etc., which is inevitable when a calomel electrode is employed. By a simple manipulation of the stopcocks an unbroken liquid connection is made with the normal electrode.

The electrolyte used was $\frac{N}{10}$ H_2SO_4, and the temperature in all cases was carefully taken, as was also the current density applied, and the voltage across the terminals. In a given experiment, the commutator was set going, the plug of the primary circuit inserted and the time noticed. Readings were taken every half minute when necessary, at a given current density, and a curve plotted indicating the change of overvoltage with time. The current density was then increased and the time-effect again measured. A curve showing the effect of current density on overvoltage (at the expiration of a given time interval) was thus obtained.

The cadmium cell employed was carefully standardized against an instrument of the Cambridge Instrument Company.

Factors affecting Overvoltage—Effect of Time of Application on the Polarizing Current.—Roczkowski* noticed that the back e.m.f. at constant current density and temperature was greater, the longer the time during which the polarizing current had been applied. This occurs even with a plate of platinized platinum, though by employing a thin film of platinum on glass the time factor disappears.

This effect of time may be due to the fact that the gas accumulated within, and at the surface of the electrode, may exert a condenser effect, the potential of the condenser increasing with time, whilst a further possibility is that the condition of the surface, or the whole physical condition of part of the metal, may be changed, which, as will be seen later, would affect the overvoltage.

Concentration polarization may also exert a disturbing effect. In this connection, a plate of platinized platinum was wrapped in filter paper to act as a diaphragm, and a high current density applied. The value of the back e.m.f. rose rapidly with time, and this increase returned to its former value on its removal. A porous diaphragm was also used, but this caused no appreciable effect, and thus probably no concentration polarization occurred.

A few previous observers have noticed that there was often a sudden change of the back e.m.f. with time, probably due to the reduction of an oxide. In one case of a platinized platinum plate observed by the author, there appeared to be a periodic increase and decrease with time at constant current density.

Tafel,† excluding the anolyte, found that a maximum polarization with time was obtained almost at once with platinum. With Cu, Bi, and Au the

* *Zeit. Phys. Chem.*, 15, 276, 1894. † Ibid., 34, 193, 1900.

back e.m.f. continued for hours, and with polished platinum a maximum could not be obtained. On addition of the anode liquid a fall of the polarization voltage was noticed. It is a matter of choice as to what period of time shall elapse, after the commencement of each experiment, at which overvoltages may be compared. In most cases the back e.m.f. approached a maximum after 30 minutes with high current density. By extrapolation the limiting value was obtained, which in the experiments of the author was taken as the overvoltage at a given current density.

The Case of Platinum and its Cathodic Polarization Potential.—Many previous investigators have assumed that the back e.m.f. from platinum was constant, irrespective of current density, and other factors. However, as

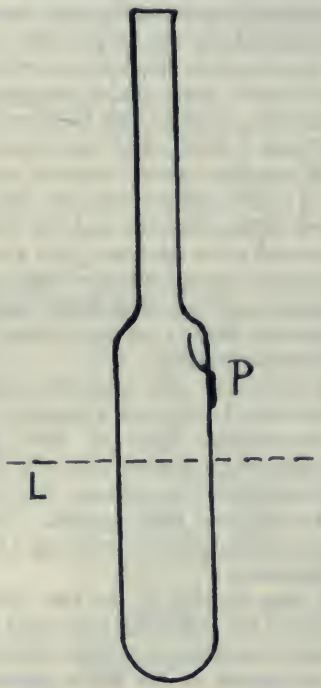


DIAGRAM II.

this changes both with time, current density, etc., it is necessary to carefully consider the behaviour of a platinized platinum plate under various conditions. This was undertaken in the present work as follows: Clean polished platinum (cleaned by electrolysis in dilute KCN and washing) was platinized carefully by electrolysis, the electrodes washed, allowed to stand, and short-circuited. The value of the back e.m.f. was then found in $\frac{N}{10}$ pure H_2SO_4.

The electromotive activity was found to change with increase of time and current density. An electrode was then prepared by depositing platinum on Jena glass from a mixture of an essential oil (lavender) with platinic chloride and a little alcohol. This was brushed over the well-cleaned electrode and heated uniformly, first to dry the oil, when on further heating a brilliant film of platinum was produced on the glass. This was then heated in the oxy-hydrogen flame so as to oxidize any carbon present, remove impurities,

and to fuse the platinum on to the glass. A rigid film of platinum was thus obtained, which was not removed in water or acid. The electrode was of the shape indicated in the figure, connection being made with the film by means of a platinum wire fused through the tube at P and fused to the surface of the glass previous to platinizing, whilst connection was made internally by means of mercury.

In no case was the electrode immersed above the level L, and so the disturbing effect of the platinum wire was eliminated. On testing this electrode the back e.m.f. was found to be constant with time, but changed with current density. A curve was drawn for this change with current density at a constant temperature.

This constancy of potential with time makes this electrode a useful standard for comparison, and a clearer idea of the change of overvoltage of other metals with time is therefore obtained.

The question now arises as to how the overvoltage shall be calculated. Since by the definition we are measuring in what degree the power of certain metals exceeds that of platinized platinum to give a back e.m.f., in the present work the overvoltage will be taken as the difference between the value of the back e.m.f. obtained with a given metal at a definite temperature and current density (after 30 minutes) and that of the platinum-glass electrode above, at a corresponding current density and temperature.

Current Density.—This effect is very marked in all cases. We may have two values according as the current density is increasing or decreasing. In the case of the platinum electrode above, this of no moment, but with solid metallic plates a definite "hysteresis" effect is noticed.

Nature of the Electrolyte.—The effect of concentration and nature of the acid does not appear to exert much effect, but this matter requires further investigation, as does also the effect of adding foreign agents to the electrolyte, such as colloids and poisons. It has been stated by Le Blanc that an increase in overvoltage is brought about by alkaloids, such as brucine, etc. It is hoped that the investigations of the effect of colloids on overvoltage will throw some light on their effect on the nature of metallic deposits obtained by electro-deposition.

Nature of the Electrode.—According to Tafel, the values for the cathodic overvoltage given by the different metals may be arranged in the following order of magnitude :—

$$Hg \longrightarrow Pb \longrightarrow Cd \longrightarrow Sn \longrightarrow Bi \longrightarrow Au \longrightarrow Ni - Pt.$$

It has been shown * that cathodic overvoltage is influenced largely by the physical condition of the metal, the degree of hardness, and previous treatment, such as electro-deposition at different current densities.

The physical nature of the metal appears to affect other properties which appear to be allied to overvoltage. Thus Graham found that the amount of hydrogen occluded by platinum depends on the texture of the sample employed, and on its previous treatment. Thus platinum sponge adsorbs ten times the quantity of gas which an equal amount of platinum adsorbs.

Effect of Thickness of the Metal.—The effect of thickness on overvoltage has been investigated by Pring† by depositing films of metal of varying thicknesses on cathodes of different metals, and finding the overvoltage of the duplicate plate thus formed. Taking any one case, say lead deposited electrolytically on a nickel cathode, it was found that the overvoltage rose

* Pring and Curzon, *Trans. Far. Soc.*, 7, 237, 1912.
† *Zeit. Elektrochem.*, 19, 255, 1913.

with increasing thickness of lead until a maximum was reached. This was assumed to be that thickness up to which the gas absorbed by the electrode exerted an effect on the polarization voltage. In the case of platinum this depth of metal appears to be approximately 4×10^{-6} mm.

In this connection the writer made a series of experiments by "sputtering" a metal on to a glass electrode, by placing the same near the anode (of the same metal as was required on the glass) in an exhausted cathode-ray tube and passing a strong discharge.

Excellent deposits of microscopic thickness were obtained, but these invariably peeled off the glass when employed in the electrolytic vessel.

Pressure.—It is expected that pressure will have a considerable effect on overvoltage, and data obtained from such measurements would be of value.

Theories of Overvoltage.—The whole question is intimately related to the processes operative in electrolysis during the transition of a gas from the ionic to the molecular condition. With regard to the main theories which have been put forward to account for overvoltages, Nernst considers that before the ions deposited at an electrode can combine to form free molecules, they must first enter within the electrode, where we have the following equilibrium, the free hydrogen then escaping:

$$2H \rightleftarrows H + H \rightleftarrows H_2.$$

With certain metals, on account of their low occlusive capacity for gases, a high e.m.f. must be applied before the gas can be forced within the electrode, which fact would explain the existence of high decomposition voltages which certain metals possess.

Tafel holds a view somewhat similar to that of Nernst, but considers that the processes taking place within the electrode require time for their completion. An excess of $H^{\cdot}$ ions thus accumulates at or within the electrode, which in turn act electromotively, giving rise to a polarization potential.

With metals such as have a low overvoltage, the metal itself exerts a catalytic effect on the above reaction, whereby the velocity of re-combination of ions is accelerated. This velocity of reaction reaches a maximum in the case of platinized platinum.

Bose* considers that the polarization e.m.f. is due both to the activity of the ions accumulated in the electrode and to that of the ions formed from the neutral gas. Its magnitude is proportional to the difference in velocity between the formation of new ions and the re-combination of the ions deposited by electrolysis to form neutral gas molecules.

Overvoltage is therefore proportional to the power of the metal for affecting this velocity of reaction.

Reichinstein† has contributed largely to this subject. He considers that the depth to which the deposited ions, and the free gas molecules formed from these, penetrate into the electrode has a definite value, and conditions the size of the "electrode volume"—which he considers to be the determining factor of overvoltage—in so far as electromotive activity is only caused by reactions taking place within this volume. The greater the volume the less is the tendency for the ions to combine, and therefore the greater is the polarization potential.

Application of Overvoltage.—Of the numerous instances where a particular property of a metal may be attributed to its overvoltage may be mentioned the effect of the nature of the electrode employed on the efficiency of an electrolytic oxidation or reduction process; and the possibility of separating

* *Zeit. Phys. Chem.*, **34**, 701, 1900.

† Ibid., **15**, 704, 1909; *Zeit. Elektroch.*, **16**, 916, 1910; **17**, 85, 1911.

two metals in solutions, whose decomposition voltages are almost equal, by choosing as cathode a metal which gives to hydrogen a decomposition voltage intermediate between that of the two metals to be separated.

In the case of the corrosion of a metal its overvoltage may be of importance as either—

(*a*) Having a tendency to retard the deposition of hydrogen or oxygen on its surface, which might either assist or prevent corrosion ;

(*b*) By setting up a high back e.m.f., which would diminish the effect of a decomposing current in cases of corrosion due to electrolysis ;

(*c*) By assisting or preventing the solution of a metal. The part played by overvoltage in this case is made clear by considering the condition which must hold in order that a metal may dissolve in an acid and evolve hydrogen. This is given by the relation—

$$\text{E.M.F. of metal} - \text{back e.m.f. of hydrogen} > \eta$$

where η = overvoltage of metal.

It is clear therefore that if η is large, no solution of the metal can occur. This is apparent with amalgamated zinc, where, owing to the high overvoltage of the mercury, no solution of the zinc takes place, the alloy assuming the overvoltage of the external metal. Similarly iron covered with zinc or tin does not rust, since η is raised.

Zinc covered with platinum dissolves readily, since η is lowered. As a means of preventing corrosion, and therefore of raising the overvoltage of the metal in question, it is necessary to coat this with either lead, tin, cadmium, or zinc, which metals have high overvoltages. The reason for the extensive employment of zinc and tin for this purpose is therefore apparent.

An accurate investigation of the effect of temperature and pressure, of the influence of colloids and poisons, and of the effect of using thin films of metal deposited on glass, will no doubt help to explain more fully the rôle played by overvoltage in the above cases.

According to present conceptions, overvoltage is simply a manifestation of the difference of the rate of production of ions and the combination of these to form complexes. Probably after being discharged the ions pass into a metastable condition and give rise to a back e.m.f. The catalytic action of the electrode is probably an important factor as affecting this velocity of reaction, and the difference in catalytic activity of various metals under different conditions of texture, temperature, etc., would explain why the value of the overvoltage varies largely with different metals. Considering the intimate relation between the above and the mode of discharge of ions in gases, experiments in this connection would appear to be of importance.

In view of the absence of any suitable factor to indicate the tendency of a metal to corrode, future experiments may indicate a parallelism between the overvoltage of a metal and its corrosion factor.

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NOTE ON A SPECIMEN OF ANCIENT IRON FROM CEYLON.

By WALTER ROSENHAIN, B.A., D.Sc., F.R.S.

(From the National Physical Laboratory.)

(*A Contribution to a* General Discussion *on* "The Corrosion of Iron and Steel," *held before a Joint Meeting of the Faraday Society and the Society of Chemical Industry at the Manchester School of Technology, Friday, April* 4, 1913.)

The specimen of iron referred to in the present note was sent to the author by Professor W. W. Haldane Gee, with the suggestion that since it was of ancient Sinhalese origin a careful examination might be of interest in connection with the subject of the corrosion of iron and steel. The specimen, which weighed about 17 grams, was described as being a portion of a link from a chain which had hung in the open air in Ceylon for a long time, probably over two thousand years, and the comparatively good state of preservation of the iron was regarded as indicating that the material was specially resistant to corrosion. Actually, although the specimen was found to be coated with a non-metallic substance largely consisting of oxide of iron, a considerable section of the material was undoubtedly uncorroded iron.

In regard to its exceptional power of resisting corrosion, this specimen is analogous to the material of the famous iron pillar at Delhi, while it also resembles in this respect the specimen of ancient Sinhalese iron described by Sir Robert Hadfield, F.R.S., in a paper to the Iron and Steel Institute in 1912.* It is interesting to note, however, that in spite of the non-corrosive properties attributed to ancient Indian iron, specimens of such iron when kept in the Museum at Colombo are described as giving trouble from their tendency to rust, and that they have had to be varnished in order to inhibit atmospheric corrosion even under the protection of a museum show-case. This observation suggests that the preservation of this ancient iron may possibly be due, not to any inherent non-corrodibility of the material itself, but to the fact that the ancient iron objects have been protected from corrosion by a coating of the nature of slag or cinder, which was probably formed on their exterior as a natural consequence of the method of manufacture used by the natives, or possibly was applied to the surface of the iron intentionally. The microscopic examination of a cross-section of the present specimen suggests that the exterior surface was completely coated in some such way, and it is quite possible that such a covering of slag or cinder may act as a very efficient preservative.

Microscopic Examination of the Iron.—Both transverse and longitudinal surfaces of the specimen were cut and polished for microscopic examination. The polished sections before etching showed a large number of black and greyish-green patches, some of which were of a duplex character, showing

* *Journal*, Iron and Steel Institute, 1912, I.

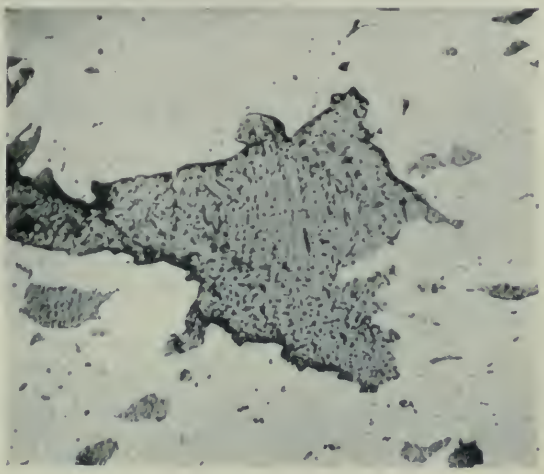

FIG. 1.—Ceylon Iron. Duplex Slag Enclosure.
Unetched. × 100.

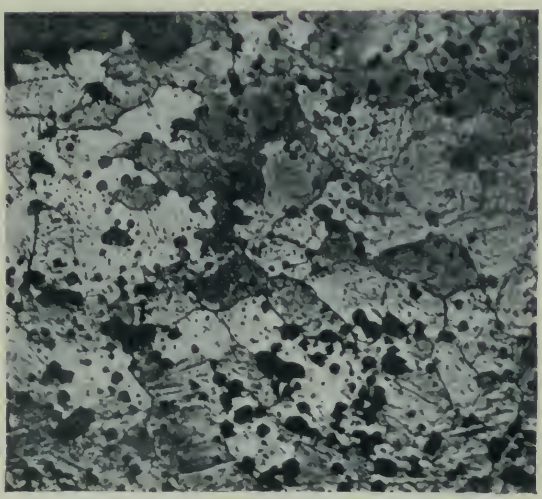

FIG. 2.—Ceylon Iron. Transverse Section.
Iodine etched. × 150.

FIG. 3.—Ceylon Iron. Longitudinal Section.
Iodine etched. × 150.

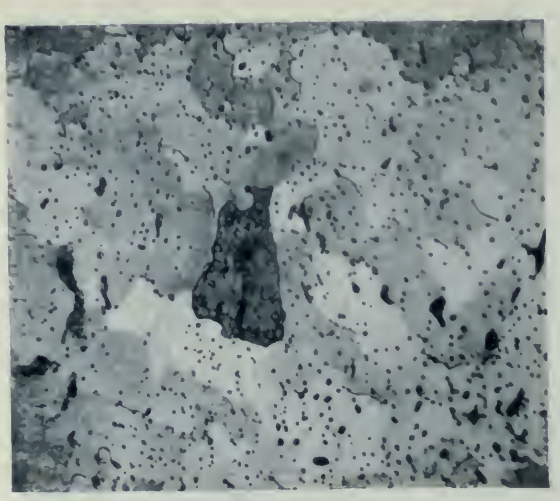

FIG. 4.—Modern Iron. Transverse Section.
Iodine etched. × 150.

FIG. 5.—Modern Iron. Longitudinal Section.
Iodine etched. × 150.

dendrites of one colour embedded in a matrix of another. These non-metallic enclosures are exactly similar in nature to the cinder or slag found enclosed in the commoner quality of modern wrought iron, except that in the longitudinal sections the slag of the modern iron is seen drawn out into much longer and finer bands than that in the ancient material, the latter occasionally showing lumps of considerable thickness even in the longitudinal sections. This difference is doubtless due to the fact that the modern iron has been rolled into bars, while the ancient specimen has probably undergone only a comparatively small amount of hammer-forging. Fig. 1 is a photomicrograph under a magnification of 100 diameters of a large slag enclosure in the Ceylon specimen showing the duplex structure.

The etching of these microscopic sections presented a point of considerable interest, as it was found that all the etching reagents employed, including iodine, dilute nitric acid, hydrochloric acid, and copper-ammonium-chloride acted upon this specimen at a very much slower rate than upon a comparison specimen of modern Staffordshire wrought iron. In this respect there can be no doubt that there is a marked difference in the chemical behaviour of the Ceylon iron when compared with modern iron, and this observation, although by no means conclusive, certainly suggests that the material itself is less corrodible than modern iron.

The appearance of the sections after etching is practically identical with that of micro-sections of modern iron. Fig. 2 is a photomicrograph of a transverse, and Fig. 3 of a longitudinal section of the Ceylon specimen, while Figs. 4 and 5 are corresponding sections of modern wrought iron. The analogy between the two is very close indeed. It will be seen that the Ceylon iron is quite free from microscopically visible carbon, thus indicating that the carbon content must be extremely low, probably not more than 0·02 per cent. The total absence of pearlite is confirmed by a systematic search over the entire area of the polished sections; in the modern iron, on the contrary, carburized patches are frequently found.

The specimen was too small in size to permit of the application of any of the ordinary mechanical tests, and observations in that direction have necessarily been confined to the determination of hardness by means of the scleroscope and of specific gravity. The scleroscope hardness was found to be 20, which approximates closely to the average value of modern wrought iron. This and other figures relating to the present specimen may be compared with the data of three specimens of Ceylon iron and of one from the Delhi pillar given by Sir R. Hadfield in the paper referred to above. The scleroscope figures given by Hadfield's specimens were 35, 44, and 23, thus indicating that Hadfield's specimens were distinctly harder than the present one. In this connection it may be mentioned that the micro-sections were examined with a view to detecting whether any cold work had been put upon the metal, and only very slight signs of deformation could be found in the crystals. In some of Hadfield's specimens cold-working is well marked, and this no doubt accounts for the difference in hardness.

The specific gravity of the present specimen was determined after cleaning the oxide and slag from the surface and subjecting the sample to a prolonged boiling in distilled water. It was then allowed to cool down in the water and the specific gravity was determined without re-exposure to the air. This procedure was necessary because the specimen was traversed by several deep fissures, no doubt due to imperfect welding, and there was some difficulty in expelling all the air from these deep cracks.

The value of the specific gravity found at 15° C. was 7·26, which is a very low figure when compared with the value for pure iron (7·84), or even com-

pared with Hadfield's specimens, which gave 7·69, 7·69, and 7·50 respectively. The imperfect welding already alluded to is no doubt responsible to some extent for this low figure, since any hollow spaces left in the metal, if completely enclosed, would not be penetrated by the water. If one ignores this possibility it is possible to calculate the percentage of oxide which must be present in order to reduce the density to 7·26, assuming that nothing but iron and oxide (Fe_2O_3) is present. This calculation requires the presence of 20 per cent. of oxide, and it was evident that such an amount could not be present. The low density is therefore no doubt attributable to hollow spaces.

In view of the observed slowness of etching of the Ceylon specimen it was thought interesting to compare it with modern wrought iron in regard to behaviour under the ferroxyl reagent of Cushman and Walker (a jelly containing phenolphthalein and ferrocyanide). A thin slice was accordingly cut from the Ceylon specimen and a similar slice was taken from a piece of wrought iron, and both were ground and polished on their surfaces, and afterwards immersed in two separate portions of the reagent. The behaviour of the two specimens was found to be very similar both as regards the extent of the action and the distribution of red and blue areas. So far as homogeneity in the electrolytic sense is concerned therefore the Ceylon specimen appears to possess no advantage over modern iron.

Chemical Analysis.—The weight of the whole specimen being only 17 grams, a complete analysis of the material was a matter of some difficulty, and special methods had to be adopted in order to obtain as complete an analysis as possible. In view of the microscopic observations indicating the complete absence of pearlite, no attempt was made to estimate the carbon, since this could only be present to a very minute extent, which may well be described as "trace" or "nil." In regard to the other elements the analysis gave the following results :—

Silicon	0·138
Sulphur	0·054
Phosphorus	0·223
Copper	0·076
Nickel	0·074
Manganese, chromium, vanadium, and molybdenum ...	Nil

For purposes of comparison the chemical analyses of the Ceylon and Indian iron given by Sir R. Hadfield are quoted here as follows :—

	Chisel.	Nail.	Billhook.	Delhi Pillar.
Carbon	traces	trace	trace	0·080
Silicon	0·12	0·11	0·26	0·046
Sulphur	0·003	nil	0·022	0·006
Phosphorus	0·28	0·32	0·34	0·114
Manganese	nil	nil	trace	nil
Copper	0·090	0·119	0·012	—

It will be seen that in most respects the present sample is very similar to those examined by Hadfield, but the sulphur content of the present sample is very high in comparison with any of Hadfield's results. Three of the latter are less than 0·006, while only one (billhook) rises to 0·022 ; the present sample

is more than double the latter. This result is of some interest, since considerable weight has been laid on the freedom from sulphur of the ancient iron in regard to its power of resisting corrosion. The phosphorus content of the present sample does not differ much from the average of the four samples given by Hadfield, while the copper content also is very similar. Perhaps the most interesting feature brought out by the analysis, however, is the presence in the iron of an appreciable quantity of nickel. It is true that this quantity is very small, but on the other hand nickel is not commonly found at all in modern wrought iron, and it is quite possible that when associated with an equal quantity of copper the two together may exert a slight inhibiting action on chemical attack; at all events, this is the only explanation of the slow etching of this specimen of iron which chemical analysis affords, and it should be mentioned that not only manganese and chromium but other elements such as vanadium, molybdenum, etc., have been looked for in the present sample. It is of some interest to consider the possible origin of the nickel content of this iron. It may of course be the case that the nickel is derived from the ores used for the reduction of this iron, and the study of those ores as now found would no doubt throw light on this point. On the other hand, there is also the possibility that the nickel may be derived from the use of meteoric iron, although as a rule meteoric iron contains much larger percentages of nickel than that found in the present sample.

The examination of a specimen of ancient iron from Ceylon which is described in the present note cannot of course claim to throw any large amount of fresh light on the subject, but such light can only be obtained by the detailed examination of a large number of specimens, and it is hoped that as a contribution in that direction the present note may be of service to those interested in the study of these relics of ancient metallurgy.

The investigation described above has been carried out in the Metallurgy Department of the National Physical Laboratory, and the author is indebted to Mr. S. L. Archbutt, F.I.C., and to Mr. W. H. Withey, B.A., for their assistance.

DISCUSSION ON "THE CORROSION OF IRON AND STEEL."

Mr. J. H. Silverwood explained, by means of lantern slides, the advantage of protective blocks in water tube ends of condensers, every tube being in electric contact with the tube plates. By this means the corrosive action, instead of attacking the tubes, travelled by the tubes to the tube plate, and on to the protector block, which alloy (being electrically positive to the material of which the tubes are composed) is more susceptible to the corrosion than the tubes, and naturally affected in consequence. The durability of the tubes depended upon the amount of corrosion taking place, but roughly, the cost of upkeep of the tube protector was about 2d. per indicated horse power per annum. He instanced, as an example of the success of the experiment, a steamer plying *via* Manchester Ship Canal between St. John's, Halifax, and Manchester. In this case the owners of the vessel were retubing the condenser, top half one year and the bottom half the following year, there being some 800 tubes in each half, and five to six tubes corroding per journey. A protective system was installed about two years ago, and so far he had not heard that a single tube had failed, this resulting in a great saving of labour and time, because when a tube gave way at sea, the result was that the vessel had to stop to take off the small doors of the condenser to plug up the leaky tube; the tube being replaced when the ship was in port.

He also instanced another protective system, working on the River Mersey, where there was a saving of about 93 per cent. of the tubes. His experience was that corrosion took place chiefly on steamers plying on estuary water, or in the case of surface condensers for electricity works or others that were using estuary water. Other instances that had come to his notice were those of the steamers *Strathmore* and *Minerva*, plying on the Clyde and practically performing the same duties, so that apparently the conditions were similar. It had, however, been found in the case of the *Strathmore*, after she had been in service for six months, that half-a-dozen tubes had failed, and then the rest followed very quickly, so a protective system was applied and a certain amount of corrosion arrested. None of the *Minerva's* tubes failed, and in order to ascertain the reason some experiments were conducted. About forty tubes were borrowed from the *Minerva* and placed in the *Strathmore*, and in the experiment they corroded. In just six weeks the first of the borrowed tubes "holed"; and in about three months, half of them had to be plugged up. The tubes were made of exactly the same metal as those in the *Minerva*, coming from the same place and being drawn at the same time. Another illustration of corrosion was supplied by three condensers belonging to the Dublin Corporation, two being badly affected, and the third remaining immune. Experiments had been made with all kinds of metals in order to ascertain results. The protective system applied was inexpensive, and was certainly a good commercial investment. In his experience, steamers plying in deep water were generally not so severely affected by corrosion, it being noticeable chiefly in the case of steamers coming into estuary water.

Mr. S. B. Freeman exhibited certain specimens of corroded condenser tubes taken out of steamers plying in both deep water and in estuary water, and showed that the resulting effect was to so weaken the tubes that they could be easily broken by the hand. The tubes were thoroughly good tubes when installed in the vessels. The ends of the tubes showed a dusty red colour, indicating that the zinc had oxidized out. In some instances corrosion had taken place in the inside of the tubes, the outer surface being unaffected owing to not coming in contact with the salt water. The greatest mischief took place when vessels were lying in port and there was a certain amount

of still water lying in the tubes and pipes. In some cases, perhaps owing to a difference in manufacture, corrosion took place in spots instead of large areas of the pipes. It would be of interest to those present to learn that Manchester Ship Canal water was excellent water to use in cases where iron and steel were necessary. He instanced the case of a steel pontoon which had lain for seventeen years in the Manchester Ship Canal, and which at the end of that period was comparatively slightly affected by corrosion. It was quite practicable to use the canal water as feed for ships' boilers, though on the other hand he was bound to confess it had seriously deleterious effects when used as circulating water through condensers and the like.

Mr. E. L. Rhead also exhibited some specimens of corroded wrought iron. Dr. Rosenhain had, he said, already remarked upon the possibility of the corrosion of wrought iron proceeding as far as the slag film which coated the fibres of the metal. He pointed out that in the production of wrought iron the material was obtained in a spongy form, consisting of separate grains adhering together, the whole of the sponge being filled with slag consisting of silicate of iron. The material was hammered in order to expel the slag and to weld the grains of iron together, but it was possible for a portion of the slag to remain and, when the iron was rolled, form a coating on the fibres. The corrosion, therefore, might possibly proceed as far as the coating, and then be arrested by the more or less continuous film of slag that was then met. He produced two specimens taken from wet gas meters, illustrating this action and demonstrating the superiority of iron under these conditions.

In most cases the difficulties encountered were not those in which the corrosion was uniform, but those in which it was confined to very small local areas. These were the most difficult cases, and he would like to know, if possible, how far electrolytic protection was likely to prevent local corrosion.

Mr. J. D. Paton said that one question which had not been answered as yet, so far as he could learn, was what was the electrolytic effect on the metal itself. It was necessary to take into consideration the internal thermic action in its relation to inherent magnetism.

Mr. W. Thomson suggested that the presence of soda as caustic or carbonate in a boiler had a considerable effect in preventing rust. He had a sample of a bright cube of iron put into a bottle containing a solution of sodium carbonate by his partner, Dr. Crace-Calvert, about thirty or forty years previously. The sample was as bright after that time as the day on which it was put in. He asked : Is it not possible that the preservative action of the electric current on the iron of boilers is due to the caustic or carbonate of soda which results therefrom ? Another point which he would suggest was to find why silicon iron did not rust at all. This alloy was about as brittle as pot, and was not of much use where strength was required, but a study of it might be useful in arriving at some satisfactory conclusion as to the nature of rusting and corrosion.

Dr. S. Wolff inquired whether the effect of strain on the various metals used in the engineering industries would tend to promote corrosion. He also produced some samples of corroded copper Grinnell sprinklers which had been forwarded to him from India, where they had been used in sheds erected for the purpose of storing jute and tea. The sheds were built on the sea-side, and during the day the atmosphere was very hot, whereas at night it became cold. It was possible that the difference in temperature might aid the corrosion shown, but he ascribed it to atmospheric influence. There were about 4,000 sprinklers used in the sheds in question, and the corrosion only attacked the vital parts where different metals were in contact, namely,

fusible metal and copper together with a name plate made of gun metal and a diaphragm. He had come to the conclusion that the salt in the atmosphere was the cause of the corrosion, as the interior portions of the sprinkler were unaffected.

Dr. W. Rosenhain began by inquiring precisely what Mr. Lambert intended by the term "physical homogeneity" as applied to metals. Except in very special cases metal was never strictly speaking physically homogeneous, but consisted of an aggregate of a number of differently oriented crystals. On any given surface these crystals presented areas having different electrolytic potentials and different solution pressures, so that strict uniformity was not obtainable even in the pure metal. On the other hand, it did not follow that the presence of impurities must produce want of homogeneity. The great majority of metals possessed a considerable power of holding in solid solution at all events small quantities of nearly every other metal, metalloid, and gas. A sample of impure zinc had been mentioned, but very probably most ordinary commercial zinc was quite as physically homogeneous as the purest zinc obtainable, because the impurities were held in solid solution, and therefore in a state of molecular division within crystals: they could not be looked for in isolated patches giving rise to electrolytic cells unless they were present in amount sufficient to exceed the limit of solid solubility. On these grounds he was inclined to the opinion that the explanation of corrodibility as due to want of homogeneity in slightly impure metals must break down.

Mr. Lambert had described experiments with commercially pure iron which had been reduced in hydrogen, and it was quite certain that this material was saturated with hydrogen. Now the amount of hydrogen present in it would depend upon the temperature of reduction and the rate of cooling, and variations in these features might thereby influence the subsequent behaviour of the iron. Another question which entered into the matter was the temperature at which the iron was reduced. In Mr. Lambert's material the metal had never been completely fused, and in this respect it resembled puddled or wrought iron, while the iron of mild steel had been completely liquid. Now it was known that iron underwent two well-defined allotropic transformations below 1,000° C., and it had recently been claimed that there was a third transformation at a very much higher temperature. It might therefore be possible that the state of molecular aggregation of iron reduced in the solid state would be different from that which had been melted. The difference in corrodibility between steel and wrought iron might be due to such a cause rather than to chemical composition as regards impurities.

Another point had been raised in regard to the possible presence of two allotropic varieties of zinc in a zinc rod, but from what was known of the equilibria of metals this seemed very unlikely except as the result of exceptionally rapid cooling. Where metal had been cold-worked one might have two modifications of the metal present, namely, the normal crystalline material and the hardened amorphous material. That would not be the case in a cast rod.

Professor Haldane Gee had referred to the peculiarity of aluminium and of some aluminium alloys in forming a protective film which gave rise to a temporary reversal of their position in the electro-chemical series. He thought, however, that it would be rash to conclude that all aluminium alloys possessed this property; in fact, he had recently found that alloys of aluminium, zinc, and copper, for instance, behaved in a way which did not suggest the formation of such protective films, while on the other hand alloys of aluminium and copper with a small amount of manganese did tend to form a protective coating.

The question of aluminium alloys brought him back to the question of the behaviour of solid solutions in regard to corrosion. Some alloys containing a

comparatively small percentage of aluminium, *i.e.*, about 10 per cent., the rest being copper, exhibit a remarkable resistance to corrosion ; samples of these alloys had been exposed to the sea for many years without suffering any appreciable loss. Since aluminium itself was regarded as exceptionally corrodible, its presence as an impurity in copper, on the basis of the theory that impurities facilitated corrosion, would lead one to expect a very different result. On the other hand, zinc in solid solution in copper was sometimes removed completely, with the result that the material became rotten, like some of the samples which had been shown that evening.

Mr. E. Ardern said that, accepting the electrolytic theory of corrosion, it would appear that the remarks of Mr. Freeman in regard to the effect of the variation of the composition of the metals touched upon the crux of the question. His own experience supported this idea, *e.g.*, he had under observation two condensers in the same steamship, one of which was tubed with brass tubes of the following composition: 68·3 per cent. copper and 31·5 per cent. zinc ; and the other with brass tubes containing 67·8 per cent. copper, 31·2 per cent. zinc, and 0·8 per cent. iron. In the case of the former condenser, practically no trouble had been experienced, while in the latter the tubes had frequently to be replaced owing to leakage caused by pitting of the metal. In this case, therefore, the presence of less than 1 per cent. of iron had apparently very considerable influence on the question of corrosion. Experiments made some years ago indicated that nickel tubes were most resistant to corrosion, but of course they were rather expensive. Mr. Ardern exhibited a seriously pitted steel boiler tube (taken from a locomotive) which had only been in use four months, working with pure town water. The explanation given by the makers of the tube was that the trouble was due to the segregation of manganese sulphide.

Professor Haldane Gee said : We must all appreciate the skilful report of Dr. Rosenhain on the sample of iron from Ceylon. He could promise a further supply of the ancient iron, so that Dr. Rosenhain would be able to extend his investigations. The more complete account of the properties of the aluminium alloys given by Dr. Rosenhain furnished a valuable guide in selecting the kind of alloy that should be used as a protector against corrosion. In reply to Mr. Rhead, experiments have been in progress at the School of Technology for some time, directed to the question of how far a composite metal that is made up of positive and negative substances in good electrical contact can be protected from corrosion when made the cathode in various electrolytes. Engineers have shown much interest in questions of corrosion. It is hoped that chemists will take a like interest, for in chemical works there is much corrosion which might be avoided or diminished by applying some of the principles discussed during the meeting.

Mr. Bertram Lambert explained that what he meant by the term "homogeneity" was that the metal was of the same allotropic form and of the same solution pressure throughout. With regard to the question of the hydrogen, the iron had been heated to 1,000° C. in a very high vacuum until spectroscopic tests showed that all the hydrogen was eliminated, the behaviour of the iron being exactly the same before as afterwards. He had also examined the possibility of an oxide film on the iron, which might have been due to the decomposition of slight traces of water in the hydrogen. The hydrogen was extremely carefully dried through long tubes containing phosphoric oxide and the behaviour was exactly the same. Further, he had thought it possible that a film of oxide might be formed on the iron when it came in contact with the water, so he brought the iron in contact with the solution of copper sulphate while it was still in an atmosphere of hydrogen. There was no difference in its behaviour.

OVERVOLTAGE.

By Professor J. W. RICHARDS (Lehigh University).

(*A Paper read before the Faraday Society, Wednesday, May 7, 1913.*)

There appears to be a misunderstanding as to what is really meant by the term "overvoltage." It was originally used by Caspari to mean the *excess* of voltage above the actual voltage absorbed in decomposition which is necessary to liberate gases upon the different metals. But many writers since then have spoken of this *excess* of voltage, or overvoltage, as if it were itself a sort of decomposition voltage, that is, as if the energy corresponding to it were absorbed in decomposition and disappeared definitely from the cell. Le Blanc, for instance (Whitney and Brown's translation), speaks of the total voltage, the sum of the real decomposition voltage, and the overvoltage as "decomposition" voltage.

The writer felt convinced *a priori* that the over-voltage did no chemical work and was therefore not of the nature of decomposition voltage. His idea was that the overvoltage was due to increased surface resistance caused by the adhesion of the gases to the metal, and to the varying degree of ease with which they collected into bubbles and left the electrode; and that the energy thus absorbed must appear as sensible heat, and not disappear as does the energy corresponding to decomposition voltage.

To test this question experimentally, an electrolytic cell containing dilute sulphuric acid was treated as a calorimeter, its water value carefully determined, and the rise in temperature caused by the passage of the current accurately observed. The amperes and applied volts being known, the total heat value of the current passed could be calculated. Subtracting from this the heat found as sensible heat by the calorimetric method, the difference was the heat disappearing in chemical work. Converting this into joules and dividing by the amperes passed, the voltage absorbed in the decomposition was obtained. The remainder of the voltage used must have been absorbed in overcoming resistance. Since the theoretical voltage absorbed in the chemical decomposition, evolving hydrogen and oxygen gas from dilute sulphuric acid, is 1·49, the question to be answered by the experiments, using different electrodes having varying overvoltages, was whether the overvoltage counted on to this 1·49 or to the resistance voltage.

Following is the condensed log of the three experiments :—

EXPERIMENT 1.

Smooth Platinum Electrodes.

	°C.
Average rise in temperature per minute	0·145
Average amperes used	1·71
Average volts applied	3·70
Average watts absorbed	6·33
Heat value of current, per minute, calories	90·73
Water value of cell, as a calorimeter	374·8
Sensible heat received, per minute, calories	54·35
Heat absorbed in chemical work, per minute, calories ...	36·38
Voltage absorbed in decomposition $\left(3{\cdot}70 \times \frac{36{\cdot}38}{90{\cdot}73}\right) =$	1·48

EXPERIMENT 2.

Smooth Gold Electrodes.

	°C.
Net average rise in temperature per minute	0·176
Average amperes used	1·73
Average volts applied...	4·13
Average watts absorbed	7·145
Heat value of current, per minute, calories	102·4
Water value of cell, as a calorimeter	374·8
Sensible heat received, per minute, calories	65·97
Heat absorbed in chemical work, per minute, calories ...	36·43
Voltage absorbed in decomposition $\left(4{\cdot}13 \times \frac{36{\cdot}43}{102{\cdot}4}\right) =$	1·47

EXPERIMENT 3.

Nickel Electrodes.

	°C.
Average rise in temperature per minute	0·145
Average amperes used	1·84
Average volts applied...	3·62
Average watts absorbed	6·66
Heat value of current, per minute, calories	95·46
Water value of cell, as a calorimeter	381·9
Sensible heat received, per minute, calories	55·38
Heat absorbed in chemical work, per minute, calories ...	40·08
Voltage absorbed in decomposition $\left(3{\cdot}62 \times \frac{40{\cdot}08}{95{\cdot}46}\right) =$	1·52

The results of these three tests give values for the voltage absorbed in decomposition which are $-0{\cdot}01$, $-0{\cdot}02$, and $+0{\cdot}03$ volt removed from the theoretical value 1·49; variations within the possible experimental error. It therefore appears as proved that the overvoltages which exist with these three metals used as electrodes have nothing whatever to do with the voltage of decomposition continuously absorbed in the electrolytic process, and that the overvoltages are simply of the nature of extra resistances, the corresponding electrical energy appearing as sensible or resistance heat.

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NEW EXPERIMENTS ON COLLOIDS.

By T. A. COWARD, B.Sc.

(*A Paper read before the Faraday Society, Wednesday, May 7, 1913.*)

Part I.—Some Effects of Dilution on Colloidal Matter.

The colloidal experiments herein described were carried out in order to find an explanation of a peculiarity observed while working with a pepsin-proteolysis.

This study in pepsin-proteolysis was being carried out in some detail in the Carlsberg Laboratory under Professor Sörensen, but the data arrived at soon showed that the arrangement of the experiment was not satisfactory. The original aim was to study the course of proteolysis when the acidity of liquid was kept at or as near as practicable to the optimum required by the peptic enzyme, *i.e.*, at an acidity of liquid in the region of P_H^+ 1·5 — 2. The extent of the changes in the digestion mixture was to be ascertained by—

(*a*) Frequent estimation of the hydrogen-ion concentration by the electrometric method.

(*b*) Frequent estimation of the formol-titratable nitrogen.

An ordinary pepsin-acid casein digestion mixture was prepared, using commercial scale pepsin, hydrochloric acid, and Kahlbaum's casein. The mixture when ready for digestion showed an acidity of P_H^+ 1·63 and a formol-titratable nitrogen content of 8·3 per cent. The mixture was placed at 37° C., and measured amounts of samples were from time to time removed. As soon as the hydrogen-ion acidity showed signs of a marked decrease, then an addition of dilute acid was made to the digestion mixture ; such additions were made in volume equal to that removed in doing the determinations above mentioned, and of acidity such that the original digestion-mixture acidity was nearly reproduced.

The first stage of this plan of experiment showed that some peculiar disturbance of the digestion mixture resulted from the dilution, but the experiment was continued on the same lines as before, until a second addition of dilute acid was made to the digestion mixture. This time there was such a marked disturbance that it was evident the experiment could not be continued on the lines proposed. The nature of this disturbance seems best shown by Table A, wherein the results of the determinations of the hydrogen-ion concentration and of the formol-titratable nitrogen are given.

The outstanding feature about the above figures is the absence of proportionality between the formol-titratable nitrogen before and after the dilution—the decrease in this figure being about four times greater than the dilution could account for in the experiment of 15/1/12. This decreased figure showed, however, almost a recovery within 24 hours, but then it was followed by a practical cessation of the proteolysis, for in 6 days only a 1 per cent. increase in the formol-titratable nitrogen was indicated.

TABLE A.

Date and Time of Determinations.	P_H^+.	Titration results stated in c.c. N/5 NaOH required per 10 c.c. of Digestion Mixture.					Percentage of Nitrogen in the Digestion Mixture. Kjeldahl determined.	Percentage of total Nitrogen that was formol titratable.
		To neutralize to Litmus.	To make pink to Phenolphthalein.	To make deep red to Phenolphthalein (*without* formol).	To make red to Phenolphthalein (*with* formol).	Total formol-titratable Nitrogen per 100 c.c.³ of Digestion Mixture.		
12/1/12 (1.30 p.m.) ...	1·63	2·80	0·20	0·15	0·45	= 0·80	0·270	8·3
,, (4 p.m.)... ...	1·64	2·95	0·35	0·25	0·45	= 1·05	0·270	10·8
13/1/12 (10 a.m.) ...	1·67	2·90	0·55	0·20	0·50	= 1·25	0·270	12·9
,, (4 p.m.)... ...	Added 140 c.c. of a mixture of 90 c.c. H_2O and 50 c.c. N/5 HCl, and after this dilution of approximately $\frac{1}{15}$ there was found:							
	1·65	2·98	0·49	0·18	0·35	= 1·02	0·250	11·4
15/1/12 (10 a.m.) ...	1·68	3·00	0·60	0·25	0·56	= 1·41	0·250	15·7
,, (2 p.m.)... ...	Added 100 c.c. of N/5 HCl and after this dilution of $\frac{1}{15}$ there was found:							
	1·55	3·40	0·40	0·30	0·30	= 1·00	0·237	11·7
16/1/12	—	3·30	0·60	0·25	0·45	= 1·30	0·237	15·3
18/1/12	—	3·30	0·60	0·25	0·50	= 1·35	0·237	15·9
22/1/12	—	3·35	0·60	0·25	0·55	= 1·40	0·237	16·4

In the *Zeitschr. für Physiolog. Chemie*, 1911, there is a paper by Professor Henriques and G. K. Gjaldbaek, wherein is noted a peculiarity in Table III, p. 369, that bears out the above fact of the disturbance of a pepsin-proteolysis when dilution is made with hydrochloric acid, but they offer no notes or remarks to explain the peculiarity.

Although the enzyme in the experiment quoted in Table A shows such an abrupt decrease of activity—almost amounting to cessation—it seemed to be improbable that partial or even almost complete destruction of the enzyme could account for the result, and that the enzyme was still active was demonstrated by the following experiment:

To 100 c.c. of the now almost stationary digestion mixture was added one gramme of casein, and after 2 days' digestion at 37° C., an increase of approximately 3·5 per cent. of formol-titratable nitrogen was found.

The above results appeared to indicate that the disturbance which a dilution with fairly dilute acid causes in a pepsin digestion mixture is not due to purely chemical reactions. In order to attempt to explain the evidently disturbed balance of such a solution, investigations were decided upon to ascertain the effects of dilution on colloidal matter, in which state both the protein and the enzyme most probably existed in the above experiments.

These new types of experiments, however, necessitated a laboratory where suitable apparatus could be found, and in the Polyteknisk Læreanstalt of Copenhagen under Assistant Knud Estrup such apparatus was available.

Although the studies thus commenced on the effects of dilution on colloidal matter are far from complete, yet the data to hand show somewhat unique phenomena to be connected with the behaviour on dilution of colloidal hydrosols.

The ordinary slit-ultramicroscope of Siedentopf and Zsigmondy was used for making the following observations, but only after some practice was it possible to obtain numbers for the submicron counts that showed the attainment of the desired accuracy. The first substance investigated was an ordinary arsenious trisulphide hydrosol. With this an attempt was made to correlate the submicron "concentration" (or the actual numbers of submicrons observable in a constant volume) and the sol dilution, but non-proportional numbers were obtained. Dilution with distilled water to five times the sol's original volume did not reduce the submicron "concentration" to one-fifth—approximately one-third of the original number of submicrons were observed.

Similar experiments were tried with a gold hydrosol, and similar results were obtained, but now the five-times diluted sol showed about one-half the number of submicrons that the undiluted sol had shown.

During these experiments it almost appeared as if different results were obtained according as to whether the dilution was made directly or indirectly, *i.e.*, whether the final sol dilution was reached at one stage by simply diluting with distilled water so many cubic centimetres of the original hydrosol to a fixed volume (direct method), or whether it was reached by stages, and a solution already containing some hydrosol was made more concentrated by addition of more sol and then diluted with water (indirect method). A considerable number of experiments showed that in the case of at least some hydrosols, when they are considerably diluted, there are produced differences in the submicron "concentrations" by these two methods of dilution. In Table B the actual figures are given, and this table also shows the scheme adopted to prove the general effect of dilution on negative colloidal matter.

TABLE B.

C.c. of original Hydrosol made up with Water to 100 c.c. of Solution.	Number of Submicrons and (in brackets) the Number of Observations upon which the Figures given in the next column are based.		Submicron "Concentration," or the Number of Submicrons observed in Volume specified.	
	By Direct Dilution.	By Indirect Dilution.	By Direct Dilution.	By Indirect Dilution.
	I. GOLD HYDROSOLS. *Observation volume, 7·64 . $10^3\mu^3$.*			
1·0	246 in (445)	117 in (216)	0·55	0·54
2·0	255 in (331)	140 in (267)	0·77	0·52*
3·0	235 in (322)	199 in (268)	0·73*	0·74
4·0	317 in (355)	374 in (369)	0·89	1·01
5·0	431 in (355)	559 in (506)	1·20	1·12
	II. GAMBOGE HYDROSOLS. *Observation volume, 6·81 . $10^3\mu^3$.*			
0·5	156 in (349)		0·44	
1·0	157 in (297)		0·52	
1·5	223 in (368)		0·61	
2·0	382 in (539)		0·71	
2·5	273 in (341)		0·80	
3·0	340 in (429)		0·79*	
	III. MASTIC HYDROSOLS. *Observation volume, 7·64 . $10^3\mu^3$.*			
0·1	311 in (454)	224 in (395)	0·68	0·56
0·2	388 in (357)	242 in (331)	0·80	0·73
0·3	371 in (342)	319 in (337)	1·08	0·94
0·4	435 in (369)	354 in (318)	1·18	1·11
0·5	602 in (387)	598 in (427)	1·55	1·40
0·75	458 in (332)	412 in (330)	1·37*	1·24*
1·0		504 in (352)		1·43
1·5		645 in (322)		2·00
	IV. ARSENIOUS TRISULPHIDE HYDROSOLS. *Observation volume, 4·88 . $10^3\mu^3$.*			
0·5	269 in (447)	145 in (188)	0·75	0·77
1·0	406 in (326)	681 in (666)	1·24	1·03
2·0	447 in (329)	264 in (210)	1·35	1·26
3·0	427 in (479)	407 in (271)	1·50	1·51

This Table B allows of the following deductions :

1. That an increase in the concentration of negative hydrosols is, at low concentrations, accompanied by an increased submicron "concentration," but such submicron increase is not proportional to the sol concentration increase ; indeed, in the examples shown there is proportional to the increasing sol concentration an actual decreasing submicron "concentration." In the case of gamboge, for example, whilst 0·5 c.c. of this hydrosol on dilution to 100 c.c. showed 0·41 submicrons per 6·8 . $10^3\mu^3$, 2·5 c.c. of it diluted to 100 c.c. showed only 0·8 submicrons in the same observation volume.

2. That at one stage in the dilution experiments with gold, mastic, and gamboge, there is with increased sol concentration an actual apparent decrease in submicron "concentration" (this stage bears the sign * in this table and also in Tables C and D that follow). Whilst these arsenious sulphide figures show no such change, its direct dilution figures exhibit greater irregularity than those of the other sols.

3. That there exists a difference between the submicron "concentration" obtained by direct dilution methods as compared with that of indirect dilution methods, although the amount of original sol is the same in the two dilutions. The data to hand, however, do not suffice for a generalized statement.

4. That decreased submicron "concentration" with increased sol concentration (already noted in 2) occurs at a different sol concentration according as to whether direct or indirect dilution methods are adopted—at least this occurred in the case of the gold sol.

The facts (3) and (4), as well as later ones in the present Paper, seem to offer some insight into the "acclimatization" phenomenon of Freundlich.

It was finally decided to continue these dilution experiments—in the case of the gold and gamboge at concentrations on each side of the point where had been noted the decreased submicron "concentration" with increased sol concentration; in the case of the arsenious sulphide between the 0·5 per cent. and 2 per cent. regions; the mastic was not further investigated, it being an ordinary commercial sample and possibly not very pure.

In Table C are shown the results of these additional dilution experiments; these sols are again referred to in Part II of this Paper.

TABLE C.

C.c. of original Hydrosol made up with Water to 100 c.c. of Solution.	Number of Submicrons and (in brackets) the number of Observations upon which the Figures given in column 3 are based.	Submicron "Concentration," or the Number of Submicrons observed in Volume specified.
	GOLD HYDROSOLS.	
	Observation volume, $6{\cdot}62 \cdot 10^3\mu^3$.	
2·0	263 in (365)	0·72
2·5	368 in (545)	0·67*
3·0	257 in (350)	0·73
	GAMBOGE HYDROSOLS.	
	Observation volume, $4{\cdot}47 \cdot 10^3\mu^3$.	
2·5	215 in (326)	0·65
2·75	149 in (276)	0·53*
3·0	195 in (303)	0·64
	ARSENIOUS TRISULPHIDE HYDROSOLS.	
	Observation volume, $5{\cdot}08 \cdot 10^3\mu^3$.	
1·0	257 in (347)	0·74
1·25	212 in (338)	0·62*
1·5	224 in (319)	0·70

This Table C shows that arsenious sulphide hydrosol does undergo, at a certain stage of dilution, a departure from the usual increase of submicron "concentration" with increased sol concentration. Table D (to be given later) shows similar results were obtained with two positive colloids.

In all these cases there was an apparent instantaneousness about this decrease of submicrons that was suggestive of electrical phenomenon, and so also were the ultramicroscopic peculiarities noted of (*a*) greater than usual Brownian motility of the submicrons just before the stage was reached at which the minimum figure was obtained, and (*b*) the greatly decreased motility and apparently greater uniformity amongst the submicrons at the point itself. Indeed, it seemed possible that the point might be that of electrical neutrality, but before deciding this more experiments were undertaken. These included a brief survey of the behaviour under dilution of two positive colloids.

The first of these to be tried was methylene blue, but at once difficulties were met. This substance at a concentration of 1 gramme per litre showed practically no light cone and very few submicrons. Then on dilution with ordinary distilled water a faint red streak appeared and only very few submicrons ; with increasing concentrations fewer submicrons became apparent. (These methylene-blue observations coincide with those previously recorded by Michaelis.) It was thus evident that the previous dilution method with ordinary distilled water was not applicable here. Then it was noted that in making the dilutions in case of the negative colloids ordinary (acid) distilled water had been used, and therefore it appeared advisable to try alkaline distilled water for the dilution of positive colloids. Ordinary distilled water was therefore rendered alkaline by adding to each litre of it 0·5 c.c. of 10 per cent. KOH. This medium was found to be not quite alkaline to phenolphthalein —for 100 c.c. of it required 0·1 c.c. of about $\frac{N}{10}$ KOH to render it alkaline to this indicator.

Methylene blue, when diluted with this (almost alkaline to phenolphthalein) water, showed both a distinct light cone and many submicrons. A series of determinations of the submicron "concentrations" at different sol concentrations were then made. A ferric hydrate sol was also similarly treated and similar determinations were made with it. Incidentally it was noted that the ferric sol on dilution with ordinary distilled water showed no light cone, although a few submicrons were discernible—the original sol, purified by dialysis, showed merely a faint streak. It appears as if the light diffracting power of some positive colloids is so similar to that of ordinary distilled water that their hydrosols are, under the ultramicroscope, practically optically void. Even the addition of a few drops of alcohol to the ferric sol at once rendered visible both a distinct light cone and submicrons

The use of even slightly alkaline water as a dispersion medium seemed open to question in the case of the ferric sol, but the figures obtained for the submicron "concentration" agreed generally with those for methylene blue In Table D (see page 148) are summarized some dilution results for two positive colloids, when the water used for dilution purposes was nearly alkaline to phenolphthalein.

Hence positive colloidal matter with an alkaline dispersion medium shows at low concentrations an increase of submicron "concentration" with increased sol concentration, and then a point where a decrease of submicrons is obtained for increased sol concentration ; subsequently, however, after a rise,* there is a decreased submicron "concentration" with increased sol concentration until finally an almost optical void stage is reached.

* The original manuscript of this Paper was revised under Dr. W. W. Taylor, Chemistry Department, Edinburgh University, and to him I herewith offer my thanks for several incorporated suggestions, and especially for his theoretical explanation of the above peculiar fluctuations of the positive submicron counts. He suggests that the figures at the assumed electrical neutrality point show aggregation phenomenon, and that the subsequent rapid rise in the "counts" is due to reversibility effects supplementing the submicrons being added in the extra sol.

TABLE D.

C.c. of original Hydrosol made up with Water to 100 c.c. of Solution.	Number of Submicrons and (in brackets) the Number of Observations upon which the Figures given in column 3 are based.	Submicron "Concentration," or the Number of Submicrons observed in Volume specified.
	METHYLENE BLUE SOLS.	
	Observation volume, $7{\cdot}64 \cdot 10^3\mu^3$.	
0·5	128 in (341)	0·37
1·5	156 in (383)	0·40
2·0	138 in (382)	0·36*
2·5	164 in (345)	0·47
3·0	230 in (429)	0·53
4·0	137 in (383)	0·35
5·0	100 in (403)	0·24
	FERRIC HYDRATE SOLS.	
	Observation volume, $4{\cdot}57 \cdot 10^3\mu^3$.	
0·5	92 in (329)	0·27
1·0	149 in (351)	0·42
1·25	119 in (345)	0·34*
1·5	194 in (364)	0·53
1·75	124 in (320)	0·38
2·5	76 in (331)	0·22

Some Experimental Difficulties.—(*a*) It was found difficult to maintain a constant room temperature from day to day. Generally speaking, however, the observations for each sol were made at the same temperature, but those of the different sols were not each made at the same. In one case in Table B, viz., that of the first five indirect dilution figures for mastic, a slight temperature difference existed between that at which the corresponding direct dilution figures were obtained. Most of the observations were made, however, at a room temperature of 18° C. The temperature of the sol in the observation chamber was determined at the time of making the submicron counts. It was noted that a 2° C. increase of temperature caused an increase of 0·1 in the submicron counts in the case of the negative sols. This amounted to a 15–20 per cent. difference in the region that these determinations were made.

(*b*) A considerable discrepancy between the submicron counts at similar sol concentrations is shown in Tables B and C. This is accounted for partly by the B and C experiments not being done at the same temperature; *e.g.*, the gamboges in C were done at 2° C. lower temperature than those in B. Also the observation volumes were not the same in the two series, and finally, most of the sols were freshly prepared when the B experiments were done, but had "aged" somewhat before the C series were prepared.

(*c*) Variation in the intensity of the arc-light illumination causes a difference of observation volume. Hence large numbers of observations are essential to establish accurate averages, and whether the 300–500 limit suggested by The Svedberg suffices or not was not proven, but presumably they do, for frequent duplicates were made in the course of the above experi-

ments ; and differences of not more than 0·02 in the submicron "concentration," or less than a 3 per cent. working error, were readily attained.

The present Paper is offered as a commencement to the study of the effects of dilution on colloidal matter, but the answer to the pepsin-digestion dilution result, which prompted these experiments, seems within view, especially if some or all of the formol-titratable nitrogen existed in the submicron form.

Some additional dilution experiments are contained in the second part of this Paper, but before passing to these, the following summary is offered as the outstanding conclusions of the present part :

1. Negative and positive hydrosols show on dilution with "acid" and "alkaline" distilled water respectively an increasing submicron "concentration" in the region of low and increasing sol concentrations.

2. Negative sols show the increased submicron "concentration" to have a fairly regular decreasing value as regards its proportionality to that of the increase of the sol concentration.

3. Both negative and positive sols show at one stage of dilution a departure from the course of increased submicron "concentration" with increased sol concentration, and this stage is assumed to be that of electrical neutrality.

4. Negative sols, beyond the point of assumed electrical neutrality, show increased submicron "concentration" with increased sol concentration.

5. Some positive sols show (at a little beyond the point of assumed electrical neutrality) a decreasing submicron "concentration" with increasing sol concentration, which decrease continues until an almost optical void is obtained.

Part II. Cataphoresis and the Coagulation of Colloidal Sols.

The cataphoretic experimental method herein adopted was as much due to Herrn Knud Estrup as to the writer ; also this investigator allowed the writer the use of a series of experimental sols, which served to provide data that considerably augment some aspects of this Paper.

The beginning of these studies was to arrange the ultramicroscope so that cataphoretic phenomena could be directly observed by it. Wires were led from the main electrical switchboard to each end of the W. Biltz type of observation chamber. By means of a voltmeter the working voltage was readily registered ; it was found that 70 volts pressure with electrodes 10 cm. apart was not generally serviceable for cataphoretic work, and mostly 220 volts was used. The insertion of one end of the thin copper conducting wire into the funnel end of the ultramicroscope's chamber offered no difficulty, but it required an upright directed piece of glass tubing to be attached to the other or clip end of the chamber to facilitate the insertion of the other wire. The ends of the two conducting wires were kept 10 cm. apart—a distance readily controlled by marks on the glass tubing of the chamber. Finally it was found advantageous to have a tapping key on the right-hand wire, and to ensure complete insulation this key was mounted on a paraffin cake. A second registering stop-watch was used to measure the time required by the submicrons to travel distances indicated by an ocular micrometer. The data thus obtained served for calculation of the velocity of the submicrons under cataphoresis, and these data seemed accurate and capable of duplication so long as the observations were made at or near the middle of the observation chamber.* Amongst other difficulties met were :

* There is one previously recorded attempt to directly determine the velocities of submicrons under cataphoresis, viz., that of Cotton and Mouton in *Comptes Rendus*, **138** (1904), pp. 1584, 1692, but practically no data are given.

(*a*) The generation of gas at the electrode ends, which gas proved non-conductive when in bubbles large enough to fill the bore of the tube wherein the electrodes were placed. It was noted that the shorter the observation periods and the lower the electrolyte-content of the sol, the less was the trouble from this source.

(*b*) The effect of the electrical current on the sol—an effect that ultimately ends in coagulation. Some considerable time is required to ensure this effect, and therefore short observation periods avoid error from this source.

(*c*) The existence of currents in the liquid under observation—which currents caused the submicrons to travel with, against, or at various angles to the direction that the electrical current imposes on them. The avoidance of considerable changes of temperature immediately before making observations, and a perfectly horizontal position of the observation chamber and its side tubes, were precautions that appeared to reduce to a minimum this type of disturbance.

The first series of observations with sols of low concentration showed that under cataphoresis the velocity of all the submicrons is not the same. This peculiarity rendered it somewhat difficult to obtain average velocity readings, especially in the case of high electrolyte containing sols. However, the range over which the velocities varied was in one or two cases determined, and in Table I these results are shown :—

TABLE I.

Hydrosol.	Sol Dilution in which the Observation was made.	Range of Velocities observed in $\frac{\text{cm.}}{\text{sec.}}/\frac{\text{volt}}{\text{cm.}}$.
Gamboge ...	1 c.c. of original sol diluted to 100 c.c. with distilled H_2O	$7{\cdot}5 - 5{\cdot}4 . 10^{-5}$
	3 c.c. of original sol diluted to 100 c.c. with distilled H_2O	$22{\cdot}7 - 14{\cdot}0 . 10^{-5}$
Arsenious trisulphide	1·00 c.c. of original sol diluted to 100 c.c. with distilled H_2O	$8{\cdot}0 - 6{\cdot}6 . 10^{-5}$
	1·25 c.c. of original sol diluted to 100 c.c. with distilled H_2O	$5{\cdot}8 - 4{\cdot}5 . 10^{-5}$

Besides proving the above indicated peculiarity this table suggests that the average velocity of submicrons under cataphoresis is not a constant, but varies according to the sol concentration. This latter statement is well supported by the following data from gamboge :

1 c.c. Gamboge sol diluted to 100 c.c. with H_2O showed a mean velocity of $6{\cdot}4 . 10^{-5} \frac{\text{cm.}}{\text{sec.}}/\frac{\text{volt}}{\text{cm.}}$.

2 c.c. Gamboge sol diluted to 100 c.c. with H_2O showed a mean velocity of $5{\cdot}2 . 10^{-5} \frac{\text{cm.}}{\text{sec.}}/\frac{\text{volt}}{\text{cm.}}$.

3 c.c. Gamboge sol diluted to 100 c.c. with H_2O showed a mean velocity of $17{\cdot}4 . 10^{-5} \frac{\text{cm.}}{\text{sec.}}/\frac{\text{volt}}{\text{cm.}}$.

Finally were examined dilutions of colloidal arsenious sulphide and of gold prepared 19 and 25 days previously, and which corresponded with the hydrosols quoted in Table C, Part I. These gave the following data :

TABLE II.

Hydrosol.	C.c. of original Hydrosol made up with Water to 100 c.c. of Solution.	Submicron "Concentration."		Mean Velocity of Submicrons under Cataphoresis $\frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt}}{\text{cm.}}$.
		Original.	After 25 days.	
Gold	2·0	0·72	0·42	$6·8 . 10^{-5}$
	2·5	0·67	0·29	0
	3·0	0·73	0·41	$6·6 . 10^{-5}$
			(After 19 days)	
Arsenious trisulphide	1·0	0·74	0·52	$7·1 . 10^{-5}$
	1·25	0·62	0·34	$5·2 . 10^{-5}$
	1·5	0·70	0·45	$6·6 . 10^{-5}$

This Table II indicates—

1. That the stage of electrical equality assumed to have been attained in the dilution experiments of Part I was so, at least in the case of the gold hydrosol.

2. That there existed in the region of electrical equality a minimum mean velocity of the submicrons when subjected to cataphoresis (see also the gamboge data between Tables I and II).

3. That a marked decrease of submicron "concentration" occurs when hydrosols are kept that are near or at the isoelectric point; such decrease is apparently correlated with the appearance of aggregated particles.

Finally, if the velocity of submicrons under cataphoresis be proportional to their electrical charge per unit of area,* then evidently by Table II and the two previous sets of data the alteration of charge that occurs in the region of the isoelectric point is a gradual and non-equalizing process. It was also noted that the direction of travel of the submicrons under cataphoresis always remained the same in the Table II experiments, hence no change of electrical sign was apparent—there was simply a gradual approach to a minimum mean charge.

The above deductions and statements receive additional support from the observations made on the borrowed sols previously mentioned. These two series of sols consisted of 40 c.c. of arsenious trisulphide hydrosol made up to a constant volume of 90 c.c. by adding the amounts of about $\frac{N}{1}$ acetic acid and of about $\frac{N}{10}$ sulphuric acid that are indicated in the first column of Tables III and IV about to be given, and then adding the requisite amount of water.

At the time of observation these series of sols had been kept for ten weeks in air-tight bottles at ordinary room temperature. In the following tables are tabulated the observation notes obtained from the sols :

* See Hardy and Harvey, *Proc. of Royal Soc., London*, September 14, 1911, p. 217.

TABLE III.

Acetic Acid Series.

C.c. of Acid used in preparing the Sols.	Light Conc.	Submicron "Concentration" per $8{\cdot}875 \cdot 10^{4}\mu^{3}$.	Velocity of Submicrons under Cataphoresis $\frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt.}}{\text{cm.}}$
5	Dim blue (1)	1·5	$6{\cdot}13 \cdot 10^{-5}$
10	"	2·0	$6{\cdot}68 \cdot 10^{-5}$
20	"	3·0	$6{\cdot}80 \cdot 10^{-5}$
30	"	4·0	—
40	—	—	—
50	Very dim blue	5·5	$7{\cdot}8 \cdot 10^{-5}$

TABLE IV.

Sulphuric Acid Series.

C.c. of Acid used in preparing the Sols.	Light Cone.	Submicron "Concentration" per $8{\cdot}875 \cdot 10^{4}\mu^{3}$.	Velocity of Submicrons under Cataphoresis $\frac{\text{cm.}}{\text{sec.}} / \frac{\text{volt.}}{\text{cm.}}$
5	Ill-defined (2)	1·2	$13{\cdot}2 \cdot 10^{-5}$
10	Only blue diffuse light	4·0	$22{\cdot}7 \cdot 10^{-5}$
20	" (3) (4)	18·0	$28{\cdot}0 \cdot 10^{-5}$
30	" (5)	1 submicron seen in about 9 secs.	—
40	" (6)	—	—
50	" (7)	1 submicron seen in about 10 min.	—

NOTES TO TABLES III AND IV.

Table III.—(1) The submicrons were variable in diffraction, and the smallest had the greatest motility.

Table IV.—(2) The submicrons were variable in diffraction.

(3) The submicrons were very variable in diffraction and size.

(4) This sol was partly coagulated.

(5), (6), (7) These sols were coagulated.

The submicrons in both Table III and Table IV always showed their direction of travel under cataphoresis to be to the positive pole.

The third sol in Table IV, or sulphuric acid series, showed incomplete coagulation, for the lower two-thirds of the sol was cloudy, and the volume of the precipitate appeared less than that in the fourth, fifth, and sixth coagulated and supernatantly clear sols.

The data in the above Tables III and IV show:

1. An increased submicron "concentration" with an increased acidity of dispersion medium.

2. An increasing velocity of submicrons under cataphoresis with an increasing acidity ; this increasing velocity continued until a maximum was attained.

3. An absence of reversal of the sign of the charge on the submicrons at and even subsequent to the presence of enough acid to cause coagulation.

4. The probable occurrence of a transformation of amicron phase into submicron phase, at least this would account for the increased submicron "concentration" noted ; the behaviour of the light cone also suggested, if less clearly, a somewhat similar conclusion.

It is apparent from the experimental evidence in this Paper that the phenomena of coagulation of colloidal sols is a rather complex process. The submicrons present do not all undergo the same change either just before or even at the coagulation point. This is especially evident from the dilution experiments of Part I, for at the electrical neutrality point in the case of the gold hydrosol only some of the submicrons coagulated at the instant that this point was reached, and in time more and more coagulated. In the last detailed experiments a somewhat similar course of changes was also seen, but especially noteworthy in these cases was the increasing presence of submicrons after, at least, considerable coagulation had occurred in the case of the third sol of Table IV, as well as the presence of submicrons in even the fourth and sixth sols. It indeed appears that when the coagulation process first begins there is inequality amongst the submicrons in the sol, and presumably the only submicrons that undergo coagulation are those that have undergone a requisite change—a change probably in part of an electrical nature. But at present it is not easy to formulate this requisite change or changes of submicrons which ensures their coagulation. In the case of the dilution experiments related herein, the submicrons show—as they approach the coagulation point—a gradually decreasing velocity under cataphoresis, whereas in the case of the addition of a strong (acid) electrolyte they show an increasing velocity towards the coagulation point. In the former case, therefore, the coagulation occurs amongst presumably minimum charged submicrons, in the latter case amongst presumably maximum charged submicrons, but in both cases amongst submicrons of the same electrical sign, although presumably bearing unequal electrical charges. Attraction and coalescence of charged submicrons bearing the same electrical sign seemed an unsurmountable difficulty, until J. J. Thomson's *Elements of Mathematical Theory of Electricity and Magnetism* was referred to. Here, in chapter v, p. 149, the possible conditions are indicated under which bodies bearing charges of the same electrical sign attract each other. Repulsion between bodies charged with electricity of the same sign only occurs if there be equality or approximate equality between the charges, but where there exists great enough inequality of charges of the same sign, then attraction may and does occur. One or two simple experiments to prove this were carried out, amongst other work, in the Physics Laboratory, University College, Dundee, where my attention was first drawn to the just quoted reference. Hence *coalescence between submicrons having the same electrical sign but presumably bearing unequal charges seems to be that which occurs in the coagulation of sols.* Undoubtedly, however, other factors contribute, *e.g.*, the constant of the dielectric (as influenced by increased or decreased presence of hydrogen ions) probably causes changes in the capacity of the submicrons and in potential, which changes predispose to coagulation or to aggregation ; also a decrease in the amicron phase may be significant of decreased frictional (?) resistance to submicron movement, and thereby

could arise increased velocity under cataphoresis and decreased retardation of aggregate formation, but these are purely hypothetical suggestions. Surface tension is another probable factor.

Finally (to return to the experiments carried out), the supernatant liquids of the coagulated arsenious sulphide sols of the sulphuric acid series, Table IV, were investigated a little; these were subjected to a rather prolonged cataphoresis, and then it was found that there had occurred:

(*a*) A disappearance of the dim blue diffuse light previously mentioned—the matrix becoming more or less dark.

(*b*) A great increase in the number of submicrons, which soon began to exhibit aggregation effects.

This latter observation shows especially that an acid-coagulation is a more incomplete process than even the previous experiments had suggested. Also it is apparent that here the amicron phase must have become submicron—a change, however, well known in colloidal investigations.* This interchange of amicron and submicron phases seems to be a rather frequent one in colloidal sols, and these experiments almost seem to suggest that a fractional coagulation method would help to explain the disturbance of the electrical equilibrium that evidently occurs in colloidal matter coagulation, although meanwhile more complete data, in respect of the electrical and other conditions of the amicron phase, are greatly to be desired.

* See W. W. Taylor, *J. of Path. and Bacteriology*, vol. 13, pp. 106–7.

A REDETERMINATION OF THE ELASTIC MODULUS OF ALUMINIUM.

By F. J. BRISLEE, D.Sc., etc.

(*A Paper read before the Faraday Society, Wednesday, May 7, 1913.*)

The modulus of elasticity of aluminium was determined by two distinct methods, viz., by the bending of a rod when supported upon knife edges at the two ends and weighted in the middle, and by the stretch of a wire, when weights are suspended at one end and the other end fixed. The bend in the first case and the stretch in the second were both measured by screw micrometers, one reading to $\frac{1}{100}$ mm. and capable of eye estimation to $\frac{1}{1000}$ mm. and a second reading directly to $\frac{1}{10000}$ of an inch.

The apparatus employed for the bending experiments consisted of a bronze clamp sliding upon a massive steel tube, down the middle of which a straight line was drawn to indicate the centre of the apparatus. The bronze clamp carried the micrometer and held it rigidly in position. Two steel knife edges were then set upon two firm supports, carried upon a brickwork column, exactly one metre apart, the metre being measured by a Whitworth standard metre, each knife edge situated exactly half a metre from the centre line of the tube bearing the micrometer clamp. The two supports and knife edges were exactly level. The aluminium bar was carefully straightened and laid on the knife edges. Exactly in the centre a knife edge carrying a scale pan was placed. The casing of the knife edge also carried a point for making contact with the micrometer. In order to tell when contact was made, the bar and micrometer were placed in series with a couple of Leclanché cells and an electric bell. As soon as contact between the micrometer and point on scale pan suspension was made, the ringing of the bell indicated the closing of the circuit. In this way it was found possible to make series of experiments showing excellent agreement for similar materials. The total deflection varied from about 2 to 12 mm., according to the diameter of the bar under test, but as a rule averaged 2–5 mm., it being important to keep the deflection small in proportion to the length of the bar and to avoid a permanent deformation.

The determination of the elastic modulus by the stretch of a wire was effected by hanging a length of 4–5 metres of wire from a solid support carried on the wall and measuring the increase in length caused by loading the end. The measuring apparatus consisted of a block of teak, which was bronze faced and fitted with a sliding centre, to which the wire under test was clamped and which carried the scale pan for the weights. The block was carried by two exactly similar aluminium wires to that under test, one on either side of the test wire. The fixed portion of the block carried a micrometer and the slider a pointer for making contact, the contact being indicated by a battery and bell, as in the bending experiments. The whole apparatus was kept in a perfectly vertical position by counterpoise weights on

each side. The general arrangements of the two pieces of apparatus are shown in Fig. 1, A and B.

A series of preliminary experiments showed that the results of the bending tests could be reproduced to within 1–2 per cent. without difficulty when repeated upon the same sample. This involved a reading which varied only in the second decimal place. A large number of experiments were made upon different material and it was found that definite differences existed, due most probably to differences in the amount of work done upon the metal. It was further found that the values obtained for the modulus of elasticity of

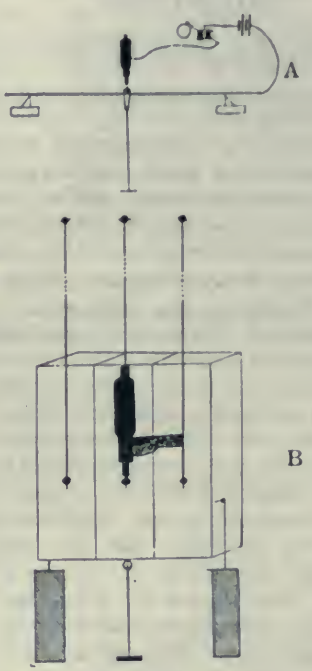

FIG. 1.

aluminium by the two methods were in good general agreement. The experiments and the results obtained will now be discussed.

SERIES I.

Bending Experiments.

The aluminium bars used in this series of determinations consisted of metal of not less than 99·25 per cent. purity. The analysis of an average sample gave :

	Per cent.
Silicon	0·35
Iron	0·28
Copper	trace
Aluminium	99·37
	100·00

The bars used were :

Square bars,	0·375 in. sq.
Rectangular bars,	0·800 × 0·436 in.
Rectangular bars,	0·876 × 0·312 in.
Round bars,	0·25 in. diameter.
Round bars,	0·375 in. diameter.
Round bars,	0·625 in. diameter.
Semicircular bars,	0·500 × 0·250 in.

The bars were as straight as possible; at least two measurements were taken, at opposite sides of the bar, so as to eliminate any residual curvature which might vitiate the results. Successive measurements with the same bar showed that the results could be reproduced to within 1–2 per cent. and frequently exact agreement between the two series was obtained. In order to avoid the effect of sudden strain, the load was put on gradually, the total load being put on in about ten steps and the deflection observed at each increment of load, an interval of three minutes being allowed between each increase of load. The results were calculated from the deflection produced by the total load, the load always being kept below that required to produce a permanent deformation.

When l is the distance between the two knife edges, a the height, and b the width of the bar, all expressed in millimetres, w the load in kilograms which produces a deflection d, then the elastic modulus is given by the formula—

$$E = \tfrac{1}{4}\frac{l^3 \times w}{a^3 b \times d}$$

for a rectangular bar. This becomes—

$$E = \tfrac{1}{4}\frac{l^3 \times w}{a^4 d}$$

for a square bar, and—

$$E = \tfrac{1}{12}\frac{l^3 \times w}{\pi r^4 \times d}$$

for a circular bar.

The results for a semicircular bar were obtained by aid of the formula—

$$E = \tfrac{1}{48}\frac{l^3 \times w}{I d}$$

where I is the moment of enertia, and for a semicircular section this is equal to—

$$I = \frac{\pi r^4}{2}\left(\tfrac{1}{4} - \left(\frac{4}{3\pi}\right)^2\right)$$

and when this is reduced, by substituting the values for π, the formula becomes—

$$I = 0{\cdot}1106 r^4$$

whence—

$$E = \tfrac{1}{48}\frac{l^3 \quad w}{0{\cdot}1106 r^4 d}.$$

The results obtained were:

Diameters.	No. of Experiments.	Highest E. Kg/mm².	Lowest E. Kg/mm².	Mean E. Kg/mm².
Square, 0·375 in.	12	6,929	6,779	6,841
Round, 0·250 in.	8	7,055	6,890	6,955
Round, 0·375 in.	14	7,133	6,848	6,973
Round, 0·624 in.	8	7,006	6,921	6,972

The rectangular bars gave different results when the bending took place along the short or long diameter, the differences between the two series being greater than the experimental error; repeated measurements on the same bar and along the same diameter did not differ by more than 1 per cent., and as a rule the difference was very much smaller than 1 per cent. The results for the two directions were:

	No. of Experiments.	Highest E.	Lowest E.	Mean E.
Short diameter	13	6,906	6,755	6,850
Long diameter	18	6,780	6,347	6,574

The semicircular bars gave the highest values of all, but were perfectly consistent in each series on the same bar. Two determinations were made upon each bar, one with the diameter of the semicircle resting upon the knife edges, the second with the circumference opposite to the diameter.

The values obtained for the modulus of elasticity from these experiments were:

	No. of Experiments.	Highest E.	Lowest E.	Mean E.
Semicircular bars	12	7,337	7,103	7,217

The semicircular bars appeared to have been somewhat overworked, and the tensile strength was not so great as might have been anticipated. The density of the $\frac{3}{8}$-in. round and square and the $\frac{1}{2}$-in. semicircular shows a variation with the elasticity, and is shown in the following table:—

Bar	$t\delta_4$.	Mean E.
$\frac{3}{8}$ in. Square	$2{\cdot}7039 \pm 0{\cdot}0001$	6,841
$\frac{3}{8}$ in. Round	$2{\cdot}7052 \pm 0{\cdot}0001$	6,973
0·5 in. Semicircular	$2{\cdot}7095 \pm 0{\cdot}0001$	7,217

The tensile strengths of these bars were determined, but, as already stated above, the semicircular bars had a lower tensile strength than would have been anticipated; but this may be accounted for by the fact that the grips used were not suitable for a satisfactory determination. The overworked state of the semicircular bars was shown by the fracture after breaking in the tensile machine and also by the microstructure.

The general mean of the results on the bars, excluding the two abnormal results, viz., for the rectangular bar along the long axis and for the semicircular bars, is—

$$E = 6{,}918 \text{ kg. per sq. mm.}$$

or—

$$E = 4{,}393 \text{ tons per sq. inch.}$$

Series II.

Stretch of Wire.

The second method used for determining the elastic modulus was to measure the stretch of a wire under a load which was gradually increased, but always kept far below that necessary to cause a permanent elongation. The wires used were all carefully selected, as uniform as possible in gauge, and free from bends and kinks. Before a set of measurements was made, the wires were fixed in position, and a weight was hung on one end which was sufficient to pull the wire perfectly straight. This was necessary in order to counteract the slight curvature caused by winding up on the block during drawing. In other cases the wires were previously straightened in a straightening machine and then suspended.

It was found that the measurements could be reproduced on the same wire to within about 2 per cent., if sufficient time were allowed to elapse between each series of measurements. If measurements were made on the same wire in rapid succession, each series was invariably higher than the preceding series, due to the after-effects of the stretch, which required a fair interval of time to regain its original length. As a rule the wire was allowed to stand for several hours before the experiments were repeated. The length of the wire used was about 4,500 mm., and the stretch between 2·5 and 4·5 mm., and the readings of the elongation were reproduced to within 2 per cent. in repeated series of measurements. From a very large number of experiments it was found impossible to reproduce the elongations more accurately than this, although, in some cases, it happened that an almost exact agreement was obtained. The diameter of the wires tested ranged from 1·692 mm. to 1·858 mm., and were drawn both upon the rapid working tandem machines through successive dies and also upon a wire-drawing block, at a much slower rate of drawing. The results of the experiments were calculated by the formula—

$$E = \frac{l \times w}{\pi r^2 \times d}$$

where d is the elongation of the wire, l the length and r the radius, all expressed in millimetres; w is the weight in kilograms, producing the elongation d.

The results are given in the following table :

Diameter of Wire in mm.	No. of Experiments.	Highest E.	Lowest E.	Mean E in Kg. per mm².
1·692	14	7,343	6,705	7,000
1·829	12	7,109	6,702	6,945
1·831	9	7,008	6,723	6,870
1·858	12	6,831	6,651	6,754

The general mean of these results is

$$E = 6{,}892 \text{ kg. per sq. mm.}$$

or—

$$E = 4{,}376 \text{ tons per sq. inch.}$$

Metal which has been overworked gives a modulus considerably higher than the above general mean. A sample of wire, 0·4266 mm. in diameter, was overdrawn to such an extent that it was impossible to bend it at right angles without fracturing. Three determinations of the modulus of elasticity upon this sample gave as a mean—

$$E = 7{,}323 \text{ kg. per sq. mm.}$$

The general mean of all the results obtained both by the bending and elongation experiments described under Series I and II, but excluding the abnormal results before mentioned, is—

$$E = 6{,}905 \text{ kg. per sq. mm.}$$

or—

$$E = 4{,}384{\cdot}7 \text{ tons per sq. inch.}$$

The experiments were made at an average room-temperature of about 17° C.

These results are somewhat lower than the results of Slotte, Katzenelsohn, and G. S. Meyer, recorded in Landolt and Börnstein's Tables,* but they represent results obtained with technical material and of a high degree of purity. The presence of an increased amount of iron, silicon, or copper would cause a considerable rise in the elastic modulus. The redetermination of the elastic modulus of aluminium was undertaken with a view to determining the comparative uniformity of the worked material regularly manufactured, and upon the whole the results show a striking agreement by both the methods of determination. The higher values are probably due to overwork and fatigue and do not represent a desirable condition for the technical metal. The passage of aluminium into the vitreous or amorphous state under the influence of work has been pointed out in a previous paper,† and that in the vitreous state the metal should possess a higher elastic modulus is to be expected.

* Landolt and Börnstein, *Physikalisch-Chemische Tabellen*, 3rd edition, p. 43, ff.
† These *Transactions*, vii., 1911, p. 221.

The further investigation of the changes is now under consideration, with a view to determining the energy of the transformation—

$$Al_{crystalline} \longrightarrow Al_{amorphous},$$

and it is hoped to communicate these results to this Society in the near future.

CHEMICAL LABORATORIES,
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THE DENSITY OF ALUMINIUM.

By F. J. BRISLEE, D.Sc., etc.

(*A Paper read before the Faraday Society, Wednesday, May 7, 1913.*)]

In a previous paper,* the author gave the results of a series of determinations of the density of aluminium, and the extremely slight change of density with work was referred to as remarkable. It was evident that the physical condition of the metal differed in specimens which had been worked in a similar manner. With a view to further elucidation of the changes which the metal undergoes under the influence of work, either rolling into sheet or drawing into wire, the investigation was continued. The aluminium used was obtained from various sources, was of high purity, and the density was determined in the cast state, as well as in the form of hard sheet and wire.

The cast metal was cut into blocks weighing 25–40 grammes each, which were filed up and then thoroughly cleansed by washing in petrol and finally in alcohol. The sheet was cut into strips about 2 in. wide and 6–8 in. long, and these strips coiled up into open spirals. The wire was coiled into very open spirals weighing from 8 to 20 grammes each. The following results were obtained :—

CAST ALUMINIUM.

Weight of Aluminium.	Loss of Weight in Water.	Temperature, °C.	Specific Gravity, Corrected.
39·1500	14·4360	19	2·7056
31·7750	11·7170	19	2·7055
32·6590	12·0430	18	2·7055
29·7340	10·9620	18	2·7067
37·7280	13·9170	17	2·7057
37·6270	13·8960	17	2·7054
39·8500	14·7020	17	2·7053
37·7710	13·9280	17	2·7066
26·2720	9·6860	17	2·7070

These results give ${}_t\delta_4$ † $= 2{\cdot}7059 \pm 0{\cdot}00044$ as a mean.

The probable error was calculated from the average error of each measurement, as obtained from the formula

$$\epsilon = \sqrt{\frac{\Sigma\delta^2}{n-1}}$$

where δ is the difference of each of the results from the mean and n the number of determinations.

* These *Transactions*, vol. vii., part 3, 1912.

† ${}_t\delta_4$ denotes the density at a mean temperature of $t°$ C. referred to water at 4° C.

The pieces of metal used in the above series of experiments were then annealed for 14 hours at 450° C. and the density again determined. The annealing was repeated for a further 14 hours, and again for a third period of 14 hours at the same temperature. The results obtained were :—

After 14 Hours' Annealing, δ Corrected.	After 28 Hours, δ Corrected.	After 42 Hours, δ Corrected.
2·7055	2·7071	2·7059
2·7056	2·7071	2·7059
2·7062	2·7070	2·7059
2·7064	2·7066	2·7059
2·7058	2·7067	2·7056
2·7060	2·7062	2·7060
2·7063	2·7066	2·7064
2·7059	2·7062	2·7058
2·7066	2·7066	2·7063

These give as means of each series—

${}_t\delta_4$ after 14 hours' annealing	2·7060 ± 0·0002
${}_t\delta_4$ after 28 hours' annealing	2·7067 ± 0·0002
${}_t\delta_4$ after 42 hours' annealing, and surfaces scratch brushed	2·7060 ± 0·0002

The general mean of the series gives—

$${}_t\delta_4 = 2{\cdot}7061$$

as the density of cast aluminium.

The metal used for this series was cut out of the middle of an 80-lb. bar of about 4 in. square. The analysis of the metal was—

	Per cent.
Silicon	0·33
Iron	0·56
Copper	trace
Aluminium	99·11
	100·00

These determinations were repeated upon a sample of much purer aluminium, but the specimens were cut from the metal near the top of the ingot. The analysis of the metal was :—

	Per cent.
Silicon	0·21
Iron	0·15
Copper	trace
Aluminium	99·64
	100·00

The density of this metal was determined in exactly the same manner as before, and the results obtained were :—

No.	Weight of Aluminium.	Loss of Weight in Water.	Temperature, °C.	Density, Corrected.
1	24·2900	8·9640	18	2·7039
2	28·3925	10·4825	18	2·7028
3	26·9566	9·9446	18	2·7049
4	31·0354	11·4524	19	2·7036
5	27·8840	10·2950	19	2·7016
6	33·2534	12·2700	19	2·7038
7	38·5250	14·2150	20	2·7027
8	33·3940	12·3240	20	2·7028
9	39·4084	14·5444	20	2·7027
10	41·4960	15·3090	21	2·7038
11	36·0990	13·3200	21	2·7027
12	31·7910	11·7340	21	2·7019

This series gives—

$$_t\delta_4 = 2{\cdot}7031 \pm 0{\cdot}0006$$

as a mean of the twelve determinations.

The specimens were then annealed for 48 hours and the density redetermined. The results obtained were :

No.	Weight of Aluminium.	Loss of Weight in Water.	Temperature, °C.	Density, Corrected.
1	24·2930	8·9660	18	2·7037
2	28·3940	10·4820	18	2·7030
3	26·9570	9·9500	18	2·7035
4	31·0350	11·4540	18	2·7033
5	27·8854	10·2964	19	2·7020
7	38·5320	14·2220	19	2·7031
9	39·4100	14·5500	19	2·7023
10	41·4970	15·3140	19	2·7035
11	36·1000	13·3280	19	2·7023
12	31·7920	11·7370	19	2·7024

Mean of the above ten results (Nos. 6 and 8 had unfortunately been lost) gives—

$$_t\delta_4 = 2{\cdot}7029 \pm 0{\cdot}0004.$$

The lower density may be due to the fact that the metal was taken from the top of an ingot. In order to find whether a difference of density existed between the metal from the top and bottom of a bar, specimens of aluminium were cut from the bottom of the ingot and as near to the crop end as possible. The results obtained were :

Ingot No. 1.		Ingot No. 2.	
Top.	Bottom.	Top.	Bottom.
2·6938	2·6997	2·6960	2·7046
2·6948	2·6998	2·6916	2·7038
2·6974	2·7003	2·6918	2·7056
2·6944	2·6992	2·6920	2·7030
2·6944	2·6979	2·6973	2·7044
2·6938	2·6990	2·6887	2·7069
2·6975	2·6990	2·6974	2·7010
2·6946	2·6997	2·6915	2·7060
2·6957	2·6985	2·6962	2·7032

Means.

Top of Ingot No. 1 ... ... $2{\cdot}6952 \pm 0{\cdot}0009$
Bottom „ „ ... ... $2{\cdot}6992 \pm 0{\cdot}0005$
Top of Ingot No. 2 ... ... $2{\cdot}6933 \pm 0{\cdot}0032$
Bottom „ „ ... ... $2{\cdot}7040 \pm 0{\cdot}0012$

Hard Rolled and Drawn Aluminium.

In order to test the effect of work upon the density of aluminium a slab of metal was rolled down from 2 in. thick to 0·018 in. thick without annealing. The sheet was then cut into strips about 2 in. wide and 6–8 in. long, rolled into loose spirals and the density determined. The results obtained were :

No.	Weight of Aluminium.	Loss of Weight in Water.	Temperture, °C.	Density, Corrected.
1	7·1654	2·6468	5	2·7085
2	9·2156	3·4040	6	2·7086
3	8·5800	3·1674	6	2·7092
4	8·7485	3·2299	7	2·7079
5	8·5578	3·1572	7	2·7099
6	7·6846	2·8360	7	2·7090
7	8·4958	3·1308	10	2·7108
8	8·2618	3·0458	10	2·7098
9	9·3180	3·4340	10	2·7107
10	7·3732	2·7182	10	2·7097
11	7·7032	2·8392	10	2·7104
12	8·2658	3·0458	10	2·7110
13	7·1654	2·6414	14	2·7087
14	9·2156	3·3976	14	2·7084
15	8·8500	3·1620	14	2·7095
16	8·7485	3·2265	14	2·7075
17	8·5578	3·1538	14	2·7095
18	7·6846	2·8326	14	2·7089
19	7·4284	2·7374	18	2·7073
20	7·9200	2·9190	18	2·7075
21	8·4260	3·1060	18	2·7071
22	5·4028	1·9908	18	2·7080
23	6·5636	2·4186	18	2·7080

The mean of these twenty-three determinations gave—

$$_t\delta_4 = 2{\cdot}7089 \pm 0{\cdot}0008.$$

The first twelve specimens were then annealed at 450° C. for 14 hours and the density again determined.

No.	Weight of Aluminium.	Loss of Weight in Water.	Temperature, °C.	Density, Corrected.
1	7·1656	2·6376	19	2·7105
2	9·2162	3·3932	19	2·7105
3	8·5802	3·1592	19	2·7097
4	8·7492	3·2212	20	2·7093
5	8·5592	3·1512	20	2·7093
6	7·6844	2·8284	20	2·7100
7	8·4980	3·1290	18	2·7101
8	8·2630	3·0430	18	2·7097
9	9·3190	3·4320	18	2·7096
10	7·7040	2·8360	19	2·7102
11	7·3740	2·7150	19	2·7097
12	8·2676	3·0446	19	2·7092

Mean—

$$_t\delta_4 = 2{\cdot}7098 \pm 0{\cdot}0003.$$

The experiments were repeated upon hard-drawn wire. A specimen of wire was used which had been drawn from 0·3 in. to 0·072 in. without annealing. The wire was carefully cleaned and made into open spirals and the density determined as before. The spirals weighed from 6 to 9 grammes each. The results obtained were :

Exp. No.	Unannealed.	Annealed at 450° C.
1	2·7029	2·7064
2	2·7032	2·7048
3	2·7036	2·7051
4	2·7017	2·7048
5	2·7025	2·7057
6	2·7024	2·7064
7	2·7023	—
8	2·7032	2·7061
9	2·7017	2·7053
10	2·7025	2·7067
11	2·7025	—
12	2·7030	2·7052
13	2·7023	—
14	2·7018	—
15	2·7029	—

These results give as means :—

Unannealed ... ... $\delta^{\circ} = 2{\cdot}7026 \pm 0{\cdot}0004$

Annealed ... ... $\delta = 2{\cdot}7057 \pm 0{\cdot}0005$

The metal was unoxidized by the annealing and practically no alteration in weight of the spirals was found after annealing. The variation only amounted to a few tenths of a milligram.

The increase in density was also found to take place when other worked forms of aluminium were used.

Some $\frac{5}{8}$-in. round rod, hard drawn, was cut into cylinders about 2 in. long, carefully cleaned, and the density determined. These were then annealed for about twenty-four hours at 450° C. and the density redetermined. The results obtained were :

Specimen No.	Before Annealing.	After Annealing at 450° C.
1	2·7049	2·7078
2	2·7054	2·7079
3	2·7057	2·7080
4	2·7053	2·7080
5	2·7058	2·7075
6	2·7054	2·7075
7	2·7054	2·7079
8	2·7060	2·7082
9	2·7060	2·7080
10	2·7058	2·7083

These results give as means :

Unannealed ... ... 2·7056 ± 0·00024
Annealed ... ... 2·7079 ± 0·00020

A hard-drawn rectangular bar 0·800 × 0·435 in. gave similar differences, but the change was not so great.

No.	Before Annealing.	After Annealing at 450° C.
1	2·7114	2·7131
2	2·7117	2·7132
3	2·7116	2·7132
4	2·7111	2·7133
5	2·7116	2·7128
6	2·7116	2·7122
7	2·7106	2·7126
8	2·7112	2·7129
9	2·7107	2·7118
10	2·7112	2·7116
11	2·7106	—

Mean—

Unannealed ... ... 2·7112 ± 0·0003
Annealed ... ... 2·7127 ± 0·0004

The work done upon the metal was apparently greatest with the 0·072-in. wire ; next on the $\frac{5}{8}$-in. rod, and least with the 0·8-in. × 0·435-in. rod, but their densities are in the *reverse* order, and all the densities increase on annealing.

Some metal of the same purity, viz. :

	Per cent.
Silicon	0·35
Iron	0·28
Copper	trace
Aluminium	99·37
	100·00

was drawn into ⅜-in. round rod, ⅜-in. square rod, and ½-in. semicircular rod, and on the draw-bench to 0·073-in. wire. The densities were then determined and the metal used for subsequent determinations of the modulus of elasticity. These will be referred to under the modulus of elasticity experiments.

No.	⅜-in. Round.	⅜-in. Square.	½-in. Semicircular.	0·073-in. Wire.
1	2·7061	2·7033	2·7089	2·7044
2	2·7042	2·7041	2·7103	2·7049
3	2·7059	2·7037	2·7102	2·7044
4	2·7053	2·7039	2·7095	2·7039
5	2·7055	2·7045	2·7091	2·7042
6	2·7056	2·7040	2·7093	2·7041
7	2·7044	2·7043	—	2·7041
8	2·7048	2·7035	—	2·7036

These results give as means :

⅜-in. square	2·7039 ± 0·0003
0·073-in. wire	2·7042 ± 0·0003
⅜-in. round	2·7052 ± 0·0004
½-in. half round	2·7095 ± 0·0002

It is evident from these determinations that the density of aluminium does not necessarily increase with the amount of work done upon it in the form of drawing into rod or wire, but that the density depends upon the state of the metal, and the operation of annealing brings about a change of state accompanied by an increase of density.

Some wire was drawn down to 0·064 in. in the hard state and its density determined ; the specimens were then annealed and the density redetermined. The results obtained were :

Specimen No.	Before Annealing.	After Annealing at 450° C.
1	2·7020	2·7052
2	2·7022	2·7052
3	2·7024	2·7055
4	2·7022	2·7047
5	2·7022	2·7056
6	2·7020	2·7056
7	2·7024	2·7048
8	2·7024	2·7049
9	2·7018	2·7047
10	2·7024	2·7048

The means of these results are :

Before annealing	$2{\cdot}7022 \pm 0{\cdot}0002$
After annealing	$2{\cdot}7051 \pm 0{\cdot}0003$

The specimens were not oxidized, the second weights differing from the first by only about 0·2 milligram as a maximum. The difference between the annealed and unannealed densities is about ten times the error of measurement.

Further experiments were made upon sheet rolled from metal of purity 99·25 to 99·5 per cent. aluminium. The analysis of the metal was :

	Per cent.
Silicon	0·29
Iron	0·38
Copper	trace
Aluminium	99·33
	100·00

The sheet was 0·080 in. thick, and was cut into rectangles weighing about 12 grammes each. After careful cleansing the density was determined ; the specimens were then annealed for 2 hours at 560° C. in an electric tube furnace, quenched, and the density redetermined. The specimens were then again annealed for 22 hours at the same temperature, and the density again measured. The results showed that the increase in density had reached its limit at the end of the first annealing. The densities are :

No.	Hard, as Rolled.	Annealed 2 Hours at 560° C.	Annealed 22 Hours at 560° C.
1	2·7076	2·7090	2·7083
2	2·7080	2·7085	2·7084
3	2·7076	2·7088	2·7086
4	2·7079	2·7082	2·7086
5	2·7076	2·7088	2·7086
6	2·7072	2·7085	2·7083
7	2·7072	2·7088	2·7085
8	2·7075	2·7082	2·7084
9	2·7073	2·7085	2·7085
10	2·7076	2·7085	2·7084

These results give as means :

${}_t\delta_4$ hard	$2{\cdot}7076 \pm 0{\cdot}0002$
${}_t\delta_4$ annealed 2 hours	$2{\cdot}7086 \pm 0{\cdot}0002$
${}_t\delta_4$ annealed 22 hours	$2{\cdot}7085 \pm 0{\cdot}0001$

No oxidation had taken place, the weight of the specimens being practically constant, and the temperature at which the density was determined did not vary more than 1° C. during any series.

It is clear from the foregoing experiments that the density of aluminium is subject to very considerable changes ; under certain conditions of work the density decreases, but increases when the metal is annealed. Such changes are not unknown, although rare, and the cases of gold and platinum, which behave similarly, were investigated by Kahlbaum and repeated and confirmed by Beilby.*

* Beilby, Institute of Metals, May Lecture, 1911.

When hard-drawn or rolled aluminium is examined under a microscope at moderate magnifications, no structure can be seen. The polished and etched specimens reveal structureless surfaces devoid of all crystalline appearance, the only distinctive feature being flow lines in the direction of work. The hard-drawn specimens which had a density higher than 2·7030 showed distinct traces of a crystalline structure, while the rectangular rod used in the experiments was distinctly crystalline towards the centre. The increase in density was always accompanied by a change in structure towards the crystalline state. Cast and slowly cooled, aluminium is very crystalline when examined under a microscope of moderate power. The process of etching aluminium which was employed will now be described.

Structure of Aluminium.

Aluminium can readily take an extremely high polish, and the polishing was done on wash-leather pads, employing a little metal polish for the initial stages and rouge for the final polishing. It was found that when it was attempted to etch aluminium specimens great trouble arose, due to pitting of the surface by the etching agent, and the real structure was obscured. A dilute solution of hydrofluoric acid was then tried and found to be most suitable for the purpose. The acid was contained in paraffin dishes, made by dipping the bulb of a flask filled with water into paraffin wax which was just melted. The dippings were repeated until a dish of sufficient thickness was obtained. When quite cold the wax dish was easily removed from the glass flask. The acid used was of such a strength that when the specimen of aluminium was immersed in the liquid a steady but not vigorous evolution of hydrogen ensued. This would correspond to about 1 part of the fuming hydrofluoric acid to 8 of water. As the etching progressed the polished surface became dark, and this darkening was removed by immersing the specimen in 60 per cent. nitric acid for a few seconds. When properly etched the surface of the specimen was of a brilliant silvery white appearance, and the structure could readily be seen under a microscope of moderate power.

In order to determine the structure of cast aluminium, an ingot was cut at right angles to its length forming a section about ½ in. thick, and then this section was cut into nine cubes, as shown in Fig. 1. The surfaces shown in Fig. 1 as shaded were then polished, etched, and photographed. The specimens were then annealed for a long time to ensure that the structure was an equilibrium structure and not influenced by the chilling effect of the iron mould in which the metal had been cast. It was found that the cast and slowly cooled structure consisted of large polyhedral crystals, which in many cases approximate to hexagons in cross section. The crystals possess a definite groundwork of a key-like formation, and have well marked crystal boundaries. The photomicrographs, Fig. 1A, Nos. 1, 7, 8, 9 show the surfaces corresponding to the shaded portions of Fig. 1. The photographs were taken of the metal as cast, and show the effects of the different rates of cooling upon the direction of crystallization.

Fig. 1A, No. 1, shows the effect of the rapid cooling of the metal by the face of the iron mould across the direction of the crystal growth. No. 7 shows the crystallization at right angles to No. 1. No. 8 is the portion where the crystallization has taken place slowest, and hence it consists of large crystals, which have grown in all directions, and not influenced to any great extent by the chill of the mould, being protected by the outer layers of metal. No. 9 shows a section at right angles to No. 8.

Fig. 2 shows the densities of the portions in a similar section, the figures in brackets being those determined from the adjacent specimens in Fig. 1.

When hard-drawn or hard-rolled aluminium in the form of rod, wire, or sheet was examined in the same way, at least two sections at right angles to

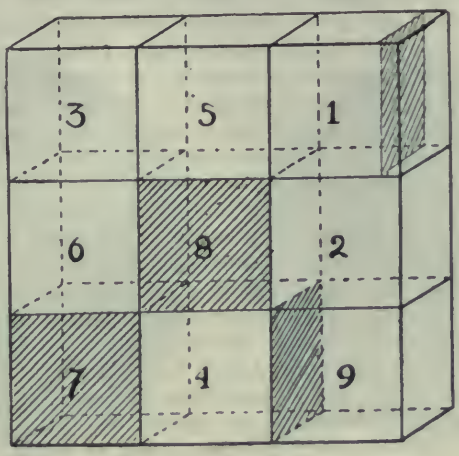


Fig. 1.

each other being prepared in every case, it was found that the crystalline structure had practically disappeared, and the appearance was amorphous, not crystalline. There were flow lines in the direction of work, but no vestige

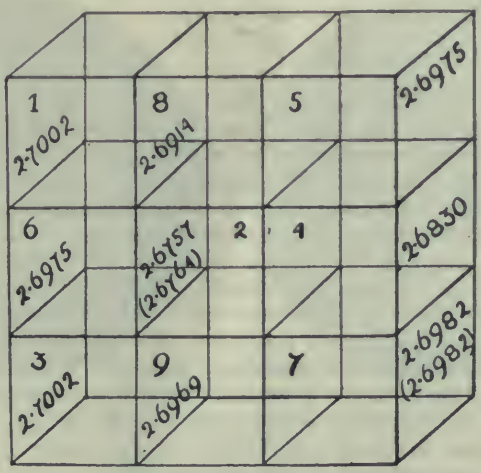


Fig. 2.

of the well marked crystal boundaries which characterize the cast structure, nor did any modification of the polishing and etching reveal the elongated crystal boundaries which are visible in other worked metals. Sections were polished and etched from a large number of different samples of worked metal which had been worked differently, and from metal of different sources,

and in all cases the effect of the work was the disappearance of all traces of crystalline structure. In hard-worked metal of large section it was found that a trace of crystalline structure remained towards the centre of the section, but the outer portions were amorphous.

The photomicrographs Figs. 3 and 4 show two sections of a hot-rolled bar, the two sections being at right angles to each other. The structure in these two shows very clearly the elongation of the crystal boundaries due to the rolling, and the crystalline structure is maintained owing to the freedom with which the molecules were able to move at the temperature of rolling, thus effecting a partial annealing. When the rolling is done cold, the crystalline structure disappears and is replaced by a granular amorphous structure, which is shown in Figs. 5 and 6, which are cold rolled, hard sheet, 0·080 in. and 0·042 in. thick respectively, and in a large number of cases examined it has invariably been found that this structure accompanies a low density. It would seem therefore that under certain conditions the effect of work upon aluminium is to change the crystalline metal into the amorphous state, and that this change is accompanied by a diminution in density. This change of density always accompanies the passage of the crystalline into amorphous modifications of other elements which are capable of existing n the two states. Johnston and Adams * have carried out accurate density determinations of metals which have been exposed to high pressures, and ascribe the changes of density to the flowing of the metal under pressure, which causes a diminution of volume owing to filling up of pores and cracks in the cast metal, the further increase of volume upon continued working being ascribed to chemical changes and change of form.

It has been further shown by Johnston † that the flowing is practically a melting, which takes place, not through the whole mass of metal, but only in the neighbouring groups of particles. Further, by application of the relationship—

$$\frac{dT}{dP} = \frac{V.T}{L},$$

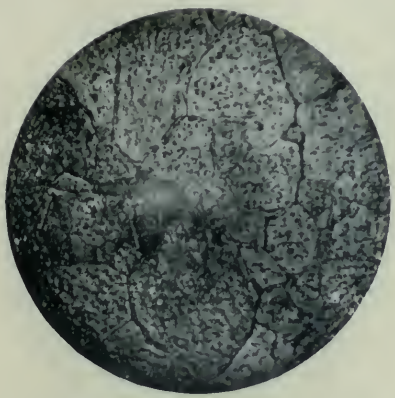
where V is the molecular volume of the solid phase, T the absolute melting-point, and L the molecular heat of fusion, the pressure necessary to lower the melting-point to the temperature of working can be calculated. It was further shown that the elastic properties of the metals and the pressures necessary to lower the melting-points to ordinary temperatures were in close relationship, and the order in each series was the same.

Tammann ‡ followed the changes produced in a metal by pressure by polishing a cube of the metal and following the changes in structure of the polished surface by means of a microscope. The compression of the metal resulted in a conversion of the polyhedra into lamellæ, the reverse change taking place when the metal is heated and annealed. The increase of volume of a metal under the influence of work is ascribed to the formation of canals and spaces by the movement of the polyhedra and by the twinning of the lamellæ. The gain in strength of the metals by working, *i.e.*, forging, drawing, or rolling, is explained by the decomposition of the crystallites into elementary crystals through the slip surfaces.

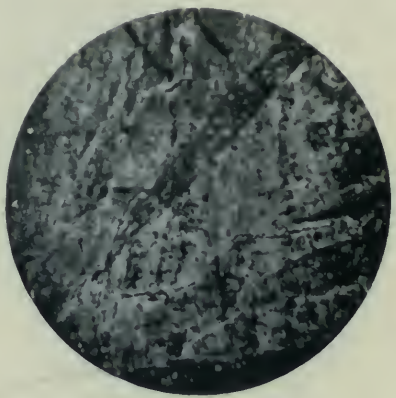
* Johnston and Adams, *Zeitschr. f. Anorg. Chem.*, **76**, 274–302 (1912); *Journal Amer. Chem. Soc.*, **34**, 563–84 (1912); *Central Blatt.*, **83**, ii., 568 (1912).

† J. Johnston, *Journ. Amer. Chem. Soc.*, **34**, 788–802; *Zeitschr. Anorg. Chem.*, **76**, 361–79 (1912); *Chemisches Central Blatt.*, **83**, ii., 569 (1912).

‡ Tammann, *Hauptversammlung der Deutsch. Bunsen Gesellschaft für Angew. Chem.* (1912); *Chem. Zeitung*, **36**, 604 (1912).



No. 1.



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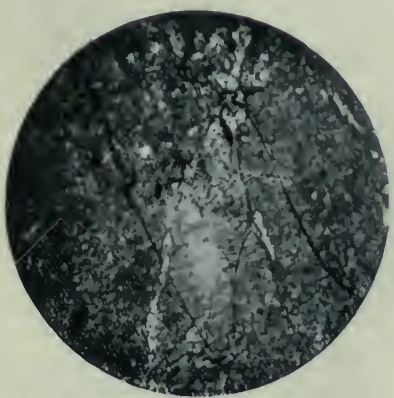

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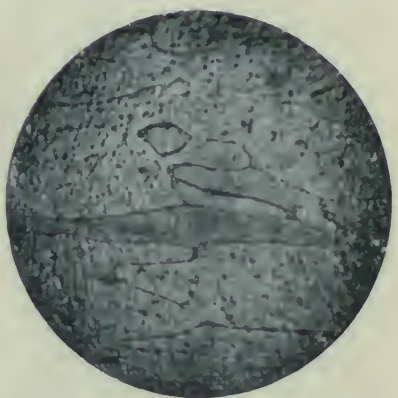


No. 9.

FIG. 1A.

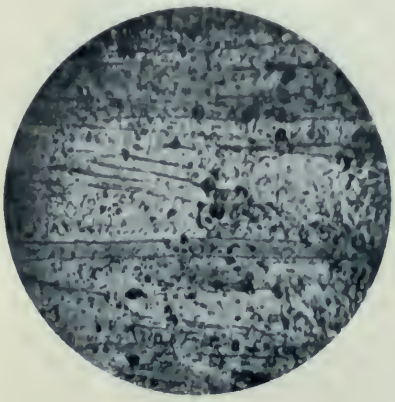


FIG. 3.

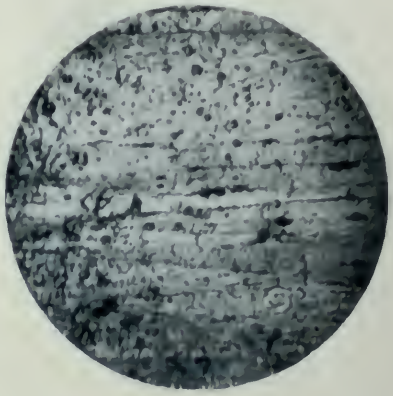


FIG. 4.

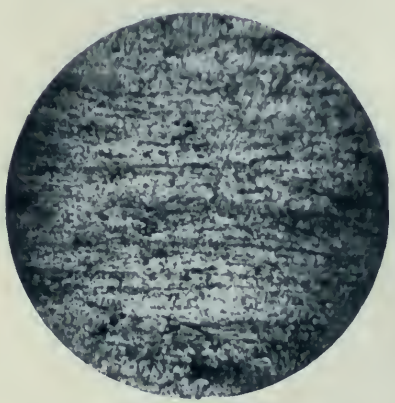


FIG. 5.

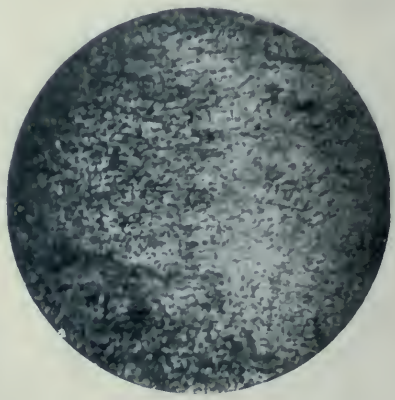


FIG. 6.

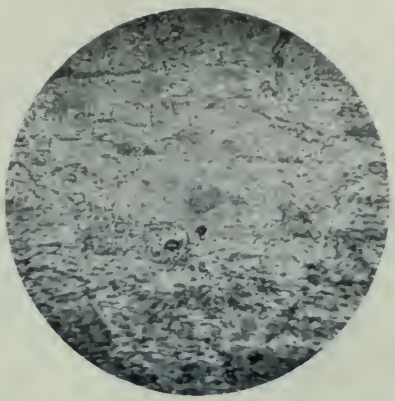


FIG. 7.—Partially Annealed Sheet, 0·042 in., 2 hours at 850° F.

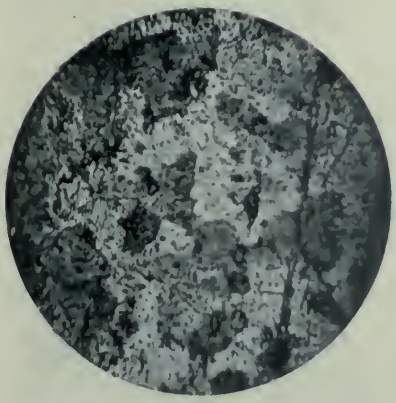
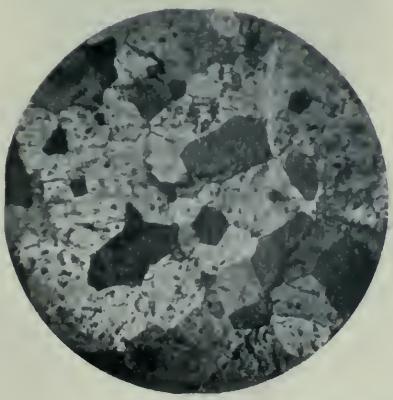


FIG. 8.—Partially Annealed Sheet, 10 hours at 850° F.

FIG. 9.—Annealed for 2 hours at 1,100° F. Still incomplete.



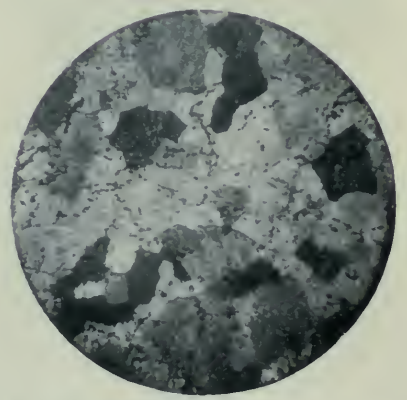
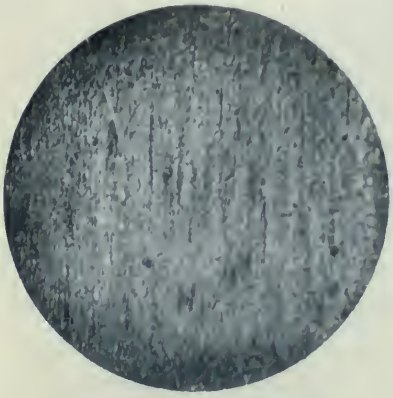
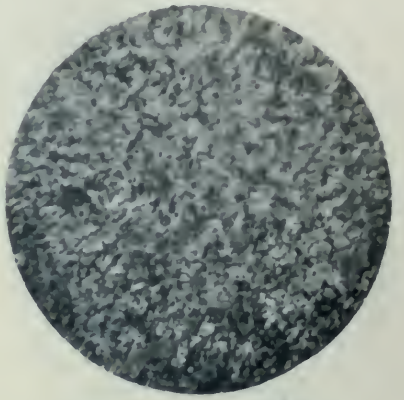


FIG. 10.—Annealed for 40 hours at 1,100° F.

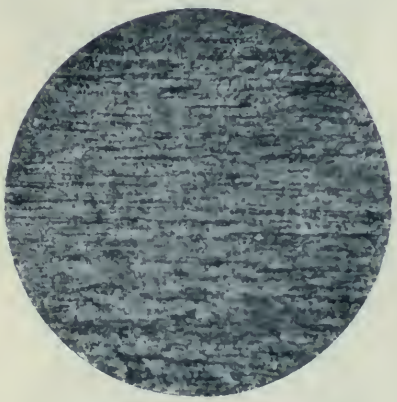


Hard-drawn Wire, 0·080 in.
Amorphous Structure. × 200.

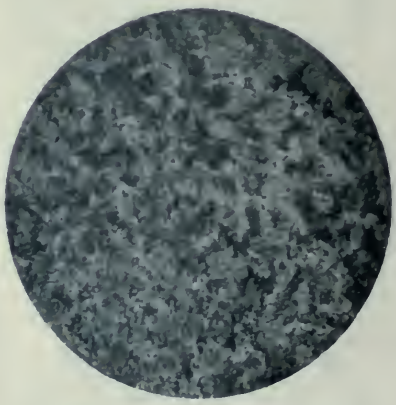


Hard drawn 0·248 in. Rod.
Cross Section. × 200.

FIG. 11.



Hard-drawn Rectangular Rod.
Longitudinal Section. Remains
of Crystallization. × 200.



Hard-drawn Rectangular Rod.
Cross Section. × 200.

FIG. 12.

In the case of aluminium, as already shown, the increase of volume with work is invariably accompanied by a disappearance of crystalline structure, the polyhedra of the cast metal passing into an amorphous or vitreous state. It would further seem as though the reverse change took place very slowly owing to the surface tension, and aluminium can be annealed so as to be soft and have an elongation of 30 per cent. against 3 to 4 per cent. in the hard state, and yet microscopically show only a very slight change in structure. These changes in structure with progressive annealing are shown in the photomicrographs Figs. 7, 8, 9, and 10, while the characteristic hard structure is shown in Figs. 5 and 6 and also in Figs. 11 and 12.

The quantitative effect of these structural changes has not yet been investigated, but the hard metal is much more readily attacked by acids than the annealed metal, as can readily be seen when etching specimens of the hard and soft state from the same sample. The difference in behaviour between hard and soft aluminium was investigated by Heyn and Bauer * in connection with the corrosion of aluminium utensils, the hard metal undergoing a much more serious disintegration than the soft when exposed to the same corroding agents.

It is evident from the foregoing results that the density of aluminium varies considerably, and that under suitable conditions the density of cast aluminium may exceed that of worked metal. It is difficult to see how the lower density of the worked metal is to be accounted for, on grounds other than a transformation from crystalline to amorphous states. Canals and spaces undoubtedly exist in the cast metal, especially in the upper portions of a cast bar, but when the bar has been subjected to hot rolling and then to cold working, these would have been closed up or greatly reduced in size, so that an increase of density should result. The existence of a vitreous, amorphous form of aluminium is also borne out by the difference between the behaviour of hard and soft aluminium in respect to corroding agents,† and the slow transformation of the amorphous into the crystalline by annealing points to the probable existence of a state of polymorphism similar to that shown by monoclinic and rhombic sulphur.

Further, density determinations, which can be made accurately to $\pm 2 \times 10^{-4}$ or $\pm 3 \times 10^{-4}$, without difficulty, form a reliable guide in the exact investigation of properties of the worked and cast metal, and are valuable aids to judging the uniformity of performance of the metal under varying conditions of use.

* Heyn and Bauer, *Mitteilung. a. d. Königl. Materialprüfungsamt*, Gross-Lichterfelde West, 29, 2 (1911).

† Heyn and Bauer, *loc. cit.*

ON THE POTENTIAL DUE TO LIQUID CONTACT.

By ALEXANDER CHARLES CUMMING, D.Sc., and ELIZABETH GILCHRIST, B.Sc.

Part III.

THE EFFECT OF VARIATIONS IN THE NATURE OF THE LIQUID BOUNDARY ON THE ELECTROMOTIVE FORCE.

(*A Paper read before the Faraday Society, Wednesday, May 7, 1913.*)

The original object of our research was to find some method by which the observed potential of a simple cell could be apportioned, with some confidence, between the diffusion potential and the electrode potential difference. The first cells examined were of the following simple type :

Hg | HgCl, 1·0 HCl | 0·1 HCl, HgCl | Hg,

with or without the use of a connecting solution between the two electrode solutions. Several difficulties arose even with this apparently simple cell, *e.g.*, the potential varied with the time the two solutions had been in contact.

Several investigators have recorded the fact that the potential of a cell in which a liquid boundary forms part of the system is not constant. Weyl * gives some data and curves showing this change of potential with time, but, beyond recording the measurements, gives little information as to the cause or conditions of the change. Lewis and Rupert † mention this effect, and state that to obtain consistent results they found it necessary to renew the boundary by running some solution out of each half-cell before each reading. This phenomenon must, in fact, be well known, as it was common knowledge in Abegg's laboratory seven or eight years ago, and the precaution mentioned by Lewis and Rupert was in general use there. This important point has received very little attention, the only investigation we have been able to find being that of Bjerrum,‡ who noted the "time change" with three cells. The potential was found to vary according to whether the boundary was sharp or mixed. Planck § deduced his well-known equation for the calculation of the diffusion potential on the assumption that no admixture of the two solutions occurs except by ionic migration. In practice, however, more or less mixing is certain to occur, and Henderson || therefore investigated the case where the two solutions are mechanically mixed at the boundary. Bjerrum ¶ calculated the diffusion potential between 0·1 KCl and 0·01 HCl and found by Planck's equation 10·7 millivolts, while Henderson's equation gave 9·4 millivolts.

* *Dissert.*, Karlsruhe, 1905.
† *Journ. Amer. Chem. Soc.*, **33**, 299, 1911.
‡ *Zeit. f. Electrochem.*, **17**, 58, 1911.
§ *Wied. Annalen*, **40**, 571, 1890.
|| *Dissert.*, Göttingen, 1907.
¶ *Zeit. für Electrochemie*, 1911, **17**, 58.

So far as we can find, this is the only case in which the Henderson and Planck equations have been compared, and it may be mentioned that both figures given by Bjerrum are about a millivolt too high. Henderson does indeed compare the two equations for one set of cells of the type

$$0{\cdot}1\ \mathrm{KCl} + x\mathrm{CH_3COOH} \mid 0{\cdot}1\ \mathrm{KCl}.$$

In these cases, however, the total potential was never as much as one millivolt, so that differences were hardly to be expected.

The two equations apply strictly to two extreme cases—Planck's to a sharp boundary at which no mechanical mixing has occurred, and Henderson's to the case where the two solutions have been so mixed at the boundary that the connecting layer may be regarded as a regular series of mixtures in all proportions. The difference between the values calculated by the two equations should give, therefore, a measure of the maximum possible variation which can be produced by differences in the nature of the boundary. As it is not possible in practice to obtain an absolutely sharp boundary, the differences observed should always be less than the calculated.

To gain an idea of the magnitude of this difference, the diffusion potentials for a number of the cells examined by Negbauer * were calculated by the Henderson equation. Negbauer's research was designed to test Planck's equation, and he gives the calculated (Planck) values for all contact potentials. Some of the data used by Negbauer have since been more accurately determined, but to save the laborious recalculation his values for ionic velocities, etc., were used in the calculations, as only a comparison was required. The Henderson equation was used in preference to that suggested by one of us, as both the Henderson and Planck equations involve the same assumptions except in regard to the nature of the boundary.

The differences found were larger than we expected, and Negbauer's numbers were therefore recalculated and many were found to be seriously incorrect.

Planck's equation for the potential between two solutions, each containing one salt with both radicals univalent, may be written

$$E_p = \frac{RT}{F} \log_e \xi,$$

where ξ is defined by the equation

$$\frac{\xi u_1 c_1 - u_2 c_2}{v_1 c_1 - \xi v_2 c_2} \quad \log_e \frac{c_1}{c_2} = \log_e \xi \quad \frac{c_1 \xi - c_2}{c_1 - c_2 \xi}$$

where u_1 and u_2 are the velocities of the kations, v_1 and v_2 the velocities of the anions, and c_1 and c_2 the corresponding ionic concentrations.

Henderson's equation for the same case may be written

$$E_h = \frac{RT}{F} \cdot \frac{c_1(u_1 - v_1) - c_2(u_2 - v_2)}{c_1(u_1 + v_1) - c_2(u_2 + v_2)} \log_e \frac{c_1(u_1 + v_1)}{c_2(u_2 + v_2)},$$

where the symbols have the same meaning as in the Planck equation.

The figures obtained are given in Table I., together with those of Negbauer. The incorrect values given by Negbauer are enclosed in brackets.

* *Wied. Annalen*, 1891, 44, 737.

TABLE I.

Concentration.		Negbauer's Figures for E_p.	E_p, Calculated by Planck's Equation.	E_h, Calculated by Henderson's Equation.	$E_p - E_h$.
HCl.	LiCl.				
0·001	0·1	0·0452	0·0452	0·0395	+0·0057
0·01	0·1	0·0307	0·0307	0·0248	+0·0059
0·1	0·1	0·0358	0·0358	0·0358	—
0·1	0·01	0·0574	0·0574	0·0650	−0·0075
0·1	0·001	(0·1154)	0·0875	0·1015	−0·0140
0·1	0·0001	(0·1731)	0·1214	0·1397	−0·0183
1·0	0·0001	(0·2308)	0·1572	0·1783	−0·0211

The difference is more clearly shown by means of the curves given below.

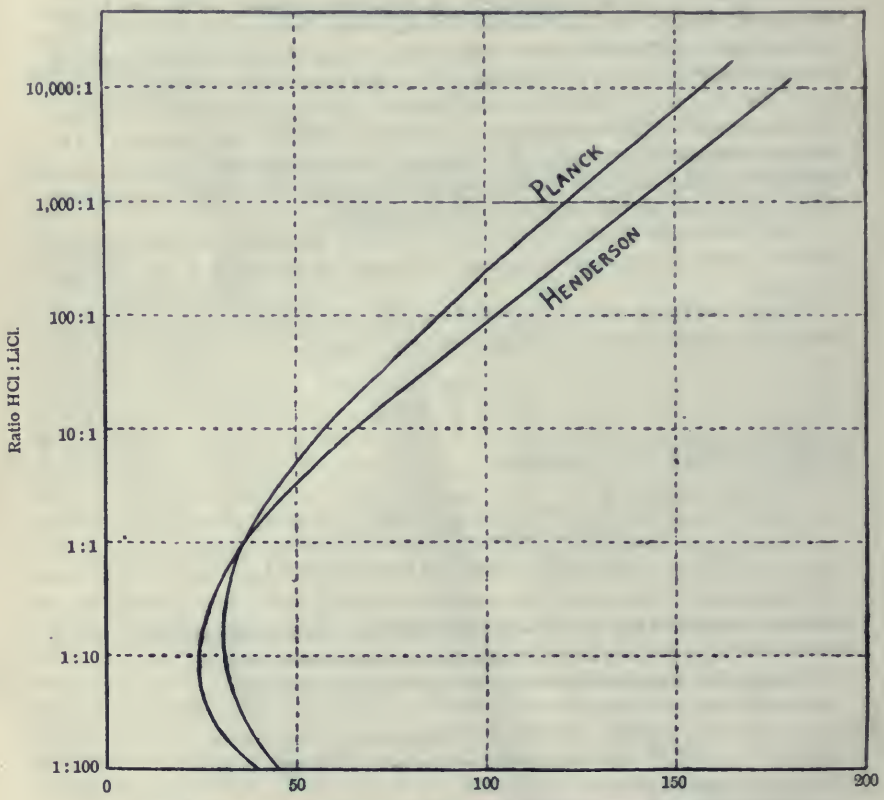


FIG. 1.—Calculated Diffusion Potential (Millivolts).

Table II gives the figures for another pair of liquids. It will be seen that Negbauer's calculations are again faulty.

TABLE II.

Concentration.		Negbauer's Figures for E_p.	E_p, Calculated by Planck's Equation.	E_h, Calculated by Henderson's Equation.	$E_p - E_h$.
HCl.	NACl.				
0·1	0·1	0·0334	0·0334	0·0334	—
0·1	0·01	(0·0561)	0·0566	0·0632	— 0·0066
0·1	0·001	(0·1152)	0·0874	0·0999	— 0·0125
0·1	0·0001	(0·1729)	0·1213	0·1382	— 0·0169
1·0	0·0001	(0·2307)	0·1572	0·1767	— 0·0195

These figures indicate that the value obtained for the diffusion potential should differ according to whether the boundary is sharp or mixed. As will be shown later, we were unable to recognize such differences of potential in practice. On the other hand, we found that the contact potential varied according to the time which had elapsed since the two solutions had been brought together—a variation which cannot be explained by the difference between a "sharp" and a "mixed" boundary.

The figures in Table III will indicate how large the change with time is in some cases. The cell under examination was

Hg | HgCl, 1·0 KCl | 1·0 HCl | 0·1 KCl, HgCl | Hg.

The half-cells used had wide side-tubes, the ends of which were *loosely* plugged with cotton-wool. (The same effect was observed without the cotton-wool.) Further details of the apparatus are given later.

TABLE III.

Time in Minutes.	E.M.F. (Millivolts.)	Time in Minutes.	E.M.F. (Millivolts).	Time in Minutes.	E.M.F. (Millivolts).
0	(67)	85	83·1	230	84·6
10	78·5	100	83·3	275	84·9
20	80	125	83·7	315	85·3
30	81	140	84·0	335	85·7
45	81·6	160	84·1	370	86·0
70	82·5	190	84·5	24 hours.	88·0

This alteration in potential was solely the result of some change in the nature of the boundary, as the normal and decinormal calomel electrodes, when in direct connection, gave the same potential (53·0 ± 0·1 millivolts) before and after the experiment.

Although in most cases it is possible to obtain concordant results by making a fresh boundary immediately before a reading is taken, this is not always the case. Sometimes, as with the above combination, no such concordance was obtained.

In view of these and similar facts it appeared desirable to investigate the effect of changes in the nature of the boundary (whether sharp, diffused, mixed, etc.) on the potential. It was decided to examine simple systems in which the electrode potential difference was eliminated by making the electrodes in all respects identical. Unless specially mentioned, each cell

was made with a pair of calomel electrodes which, by repeated tests, were found to agree to less than 0·1 millivolt.

An apparently symmetrical system was obtained if a single solution was interposed, *e.g.*,

Hg | HgCl, 1·0 KCl | 1·0 HCl | 1·0 KCl, HgCl | Hg.

No electromotive force was to be expected from this cell unless there was a difference in the nature of the two liquid boundaries.

As we shall be constantly using the terms "sharp," "mixed," and "diffused" to distinguish between three kinds of boundaries, it may be well to define what we mean by these terms.

Sharp Boundary.—We have used this term to indicate that the boundary was formed with special precautions to prevent mechanical mixing.

Mixed Boundary.—When two solutions were *mechanically* mixed at the boundary we have called this a "mixed" boundary. In our experiments the mixed layer would be at least 1 cm. in thickness.

Diffused Boundary.—At the boundary between any two solutions alterations in concentration will occur on account of diffusion.

The boundary layer formed by diffusion exhibits a different concentration gradient to that formed by mechanical mixing. Both sharp and mixed boundaries become diffused boundaries with time, but the change caused by diffusion should be more marked with a sharp boundary.

In view of the results obtained, a somewhat detailed description of the apparatus used appears desirable, as the observed potential was found to be influenced by even such a slight variation as alteration in the diameter of a connecting tube.

Experimental Details.

All measurements were made at 25°. The electromotive force was measured by the ordinary potentiometer method, using a Paul "special sensitive" galvanometer as null instrument. The galvanometer had a resistance of 390 ohms, and gave a deflection of 1,570 mm. per microampere at 1 metre. The potentiometer was made by Pye, of Cambridge, and could be read with ease to $\frac{1}{10}$ millivolt. The cadmium cell used as standard was checked from time to time against a Weston cell, the e.m.f. of which was 1·0183 volt at 20° (N.P.L. certificate).

Form of Cell Used.—At various times many types of half-cells have been used, and it is believed that all types described in the literature have been tried. The form which we prefer is the simple one described in most text-books. Our experience is that it is more satisfactory in use and less open to objection than the more complex vessels sometimes used. The dimensions, more particularly of the side-tube, have some influence on the results obtained, and are therefore given in Fig. 1 (drawn to scale, half-size). The internal diameter of the side-tube A was 5 mm. To prevent entrance of air when filling, the end of this tube was *very loosely* plugged with a small piece of cotton-wool.* If the connecting solution in B was of lower specific gravity than the solution in the cell, the end of the side-tube was fitted with a bent-up tube as shown at C. In some experiments a Nernst U-tube was used in place of the connecting vessel B.

With large numbers of cells in a thermostat clamps are inconvenient, and a simple but satisfactory stand for the cell was made from a large cork cemented by sealing-wax to a piece of lead (see D in Fig. 2). The cells stood on a tray of woven wire, and were immersed to the depth shown by the line E.

* This was found to be permissible if the plug of cotton-wool was very loose.

An obvious objection to this type of cell is that part of the side-tube is out of the bath, and is probably at a lower temperature. It is improbable that this causes any appreciable error, as it was found, in an experiment with a half-cell filled with normal hydrochloric acid, that there was no alteration in potential when the part F was cooled at least 10° below the temperature of the thermostat.

Another source of error lies in the fact that, as the vessel B was usually uncovered, the temperature of the solution in it was always slightly below that of the thermostat. The temperature difference was noted on several occasions, and was usually 0·3°, and never more than 0·5°; the error will therefore be practically negligible.

Experiments with Boundaries of Different Thicknesses.

Preliminary experiments showed, as we expected, that the use of cotton-wool or membranes at a boundary led to inconsistent results. To obtain a

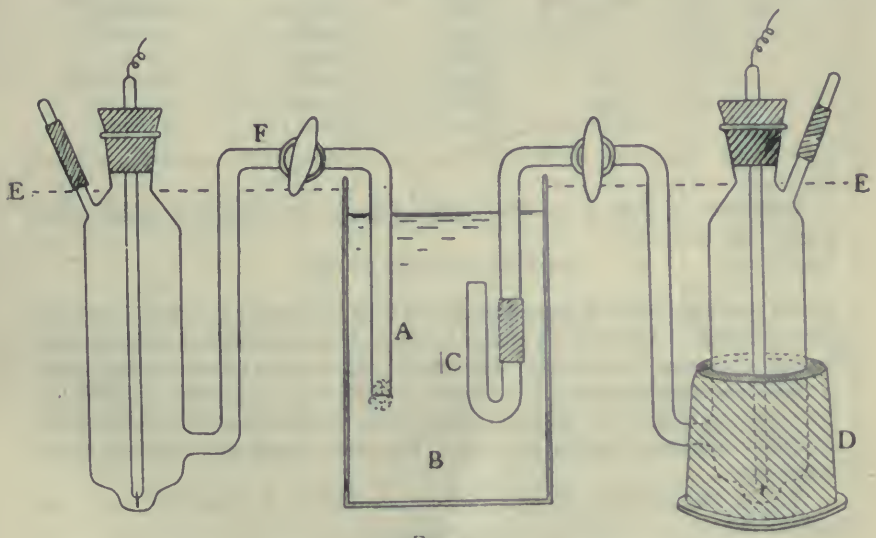


FIG. 2.

sharp boundary we therefore ran the connecting solution in below the electrode solution in a U-tube, adopting the device used by Nernst for his lecture experiment on ionic migration. In this way two sharp boundaries were obtained (To render the boundary visible a trace of dye-stuff was added to the lower solution.) The liquids were then mixed at one boundary by means of a wire stirrer.

The observed potential was usually below 0·5 millivolt, and in all cases fell quickly to zero. The solution used as connecting solution was always one which was known, from previous experience, to give marked variations of potential when in connection with potassium chloride, yet in all cases little or no potential was obtained. For example, the following cell—

$$0{\cdot}1\ \mathrm{KCl} \mid \underset{a}{5{\cdot}0\ \mathrm{HCl}} \mid \underset{b}{0{\cdot}1\ \mathrm{KCl}}$$

gave no potential, though *a* was a sharp boundary and *b* a mixed boundary. Such a cell should give a potential if the differences are to be explained by

assuming that the Planck equation is applicable to a sharp boundary and the Henderson equation to a mixed boundary. The magnitude of the potential on this hypothesis is shown by the figures in Table IV, in which are given the diffusion potentials as calculated from the two equations. The migration velocities used in the calculations were K = 74, Cl = 75, and H = 347 (for 25°).

TABLE IV.*

Ratio of Ionic Concentrations.		Diffusion Potential (Planck).	Diffusion Potential (Henderson).	Difference, $E_p - E_h$.
HCl.	KCl.			
1,000	1	0·118	0·132	— 0·014
100	1	0·0841	0·0938	— 0·0097
10	1	0·0527	0·0573	— 0·0046
1	1	0·0265	0·0265	—
1	10	0·0100	0·0085	+ 0·0015
1	100	0·0027	0·0023	+ 0·0004
1	1,000	0·0014	0·0013	+ 0·0001

Inspection of Fig. 3, in which these figures are expressed graphically, shows that the cell

0·1 KCl | 5·0 HCl | 0·1 KCl

should give a potential of several millivolts if one boundary is "sharp" and the other "mixed." Yet we were unable to obtain any potential however carefully the sharp boundary was made. To obtain a still sharper interface the density of the connecting solution was increased by addition of glucose, but still no potential was obtained. The acid solution was dyed with methyl red and the boundary appeared extremely sharp. The same result was obtained in all other cases.

Three explanations of this failure to obtain a potential may be considered :

1. That sufficient mixing had occurred at the "sharp" boundary to bring it into the category of "mixed" boundaries. It seems impossible completely to disprove this, but, if this was the case, no "sharp" boundary will ever be met with in ordinary practice, as this was prepared with special care. The mixed layer in our experiments must have been a small fraction of a millimetre in thickness.

2. That Planck's formula is not valid. This is quite possible, as Pleijel† has pointed out that one assumption made by Planck, namely, that the mixed layer formed at the boundary is of uniform concentration, is almost certainly incorrect.

3. That Henderson's formula is not valid. Henderson has himself pointed out that it was necessary to make several assumptions in order to treat the subject mathematically. All the same assumptions are, however, involved in

* This set of figures is of interest in connection with the elimination of diffusion potential by means of a connecting solution of potassium chloride or ammonium nitrate. From the curves it will be seen that it is essential that the concentration of the connecting solution should greatly exceed that of the other solutions.

† *Zeit. physik. Chem.*, **72**, 1, 1910.

the derivation of Planck's equation, but the Henderson equation is not open to the objection urged by Pleijel to the Planck equation.

It appears therefore that the "sharp" boundary to which alone the Planck equation is applicable is not realizable in practice, and that the cause of the variations observed must be sought in some other direction.

The Alteration of the Diffusion Potential with Time.

N. Bjerrum* in an interesting paper on this subject has calculated the alteration in the contact potential caused by diffusion and shown that the "time change" is inversely proportional to the thickness of the mixed layer at the boundary. Bjerrum's work appeared to us at first inconclusive, but a

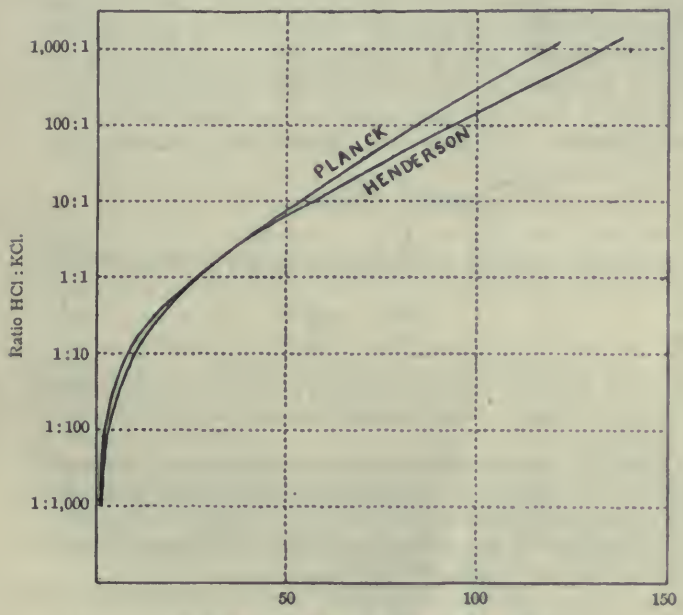


Fig. 3.—Calculated Diffusion Potential (Millivolts).

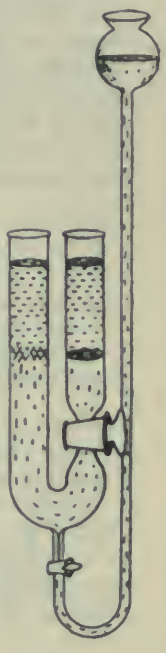


Fig. 4.

review of our own experiments shows them to be in general accord with Bjerrum's view, though there are still some points of difficulty.

Bjerrum has calculated the actual change in potential caused by diffusion for a fixed time. It was, of course, necessary to make arbitrary assumptions as to the thickness of the mixed layer, etc., but his calculations show clearly that the time change will (1) be inversely proportional to the thickness of the boundary, and (2) be of appreciable magnitude only when there are marked differences in the ionic velocities.

On these two points our experiments support Bjerrum's hypothesis. His calculations show further that the "time change" at the boundary 0·1 KCl | 0·1 HCl is small, but is larger for the boundary 0·1 KCl | 0·01 HCl. On this point our experiments disagree entirely with Bjerrum's calculations and experiments. We found that the "time change" was always more

* *Loc. cit.*

noticeable the greater the relative concentration of the hydrochloric acid (or, in general, the greater the concentration of the salt composed of ions with dissimilar velocities).

Experiments on the "Time Change."—One limb of the Nernst U-tube (Fig. 4) was fitted with a large tap and the denser connecting solution run in below the other (electrode) solution to obtain two sharp boundaries. The taps were closed and the solution removed completely from the limb bearing the tap. After from 1 to 24 hours fresh (electrode) solution was poured into this limb, the tap opened, and a sharp boundary obtained as usual. The system was thus symmetrical except that at the old boundary diffusion must have occurred to a greater extent than at the new boundary. In most experiments no potential was obtained, and in no case did the observed potential exceed 0·5 millivolt. The U-tube used in these experiments was about 1 cm. in diameter, and it seemed possible that sharper boundaries and larger effects would be obtained with narrow tubes. The experiments were therefore repeated, using the apparatus shown in Fig. 2. To the ends of a siphon tube (A in Fig. 2), a capillary tube, straight or bent into a U-tube according to the relative densities of the solutions, was attached. The capillary tube was about 1 mm. in diameter, whilst the siphon tube of the other half-cell was about 5 mm. in diameter. The following values were obtained with the cell

$$1{\cdot}0\ \mathrm{KCl} \mid \underset{a}{1{\cdot}0\ \mathrm{HCl}} \mid \underset{b}{1{\cdot}0\ \mathrm{KCl}},$$

where the boundary *a* was formed in a capillary tube and *b* in a wider tube.

Time in minutes ...	...	3	7	10	25	40	70	150
E.m.f. (millivolts)	...	0	−0·5	−0·4	−0·7	−1·0	−0·9	−0·9

The normal electrodes when in direct connection have no potential either before or after the experiment, so the observed potential was solely due to changes at the boundary.

Similar experiments were carried out with other solutions, and in every case a "time change" was observed. The magnitude of the change appears to be dependent on so many factors that the actual numbers we obtained have no special significance. It may be mentioned that the highest observed potential of this kind was 15·2 millivolts for the cell

$$0{\cdot}1\ \mathrm{KCl} \mid 5{\cdot}0\ \mathrm{HCl} \mid 0{\cdot}1\ \mathrm{KCl}.$$

Usually the potential rose slowly and steadily, but sometimes it reached a maximum value, after perhaps a day, and fell again. The effect was most marked in cases where the concentration of the salt which yielded ions of different velocities was relatively great. In general it was found that the "time change" was large where the diffusion potential was large. The elimination of diffusion potential by means of a connecting solution has therefore the practical advantage that the "time change" is also eliminated.

Influence of Diameter of Tube.—The "time change" was found to occur however the boundary was made, but was far more marked when capillary tubes were used than with wide tubes. When the boundary was made within a 1 cm. tube the "time change" was almost inappreciable, even when the original boundary was sharp and when the solutions gave a marked "time change" with narrow tubes. We believe that these differences with variation in the diameter of the tube are due to mixing of the solutions by convention currents when wide tubes are used.

It was expected that when both half-cells were fitted with capillary tubes no potential would be obtained, as the "time changes" at the two boundaries should counterbalance one another. Usually, however, a potential was observed—probably on account of slight differences between the capillaries.

The following experiments illustrate clearly the errors which may arise through this "time change." The cell under examination was

1·0 KCl | 1·0 HCl | 1·0 KCl,

and both half-cells were fitted with siphon tubes about 1 mm. in diameter. This cell gave no potential the day it was prepared. The next day the potential was + 0·7 millivolt. After running some solution out of one half-cell the potential changed to − 2·0 millivolts. On running some solution out of the second capillary the potential fell to zero.

With another cell of similar type the potential, after standing for a day, was 1·5 millivolts. After running the solution out of one capillary it became 3·5 millivolts and fell to zero when the solution was run out of the second capillary.

Is the "Time Change" due to Ionic Migration or to Salt Migration?

It is obvious that the passage of salt from one solution to another may occur by migration of salt molecules as such, by ionic migration, or by a combination of both. Bjerrum* has considered only the possibility of ionic migration, but salt diffusion must also occur except with very dilute solutions. Possibly the explanation of some of the remaining difficulties will be found in this dual nature of the diffusion process.

Some evidence in support of the idea of salt diffusion (as distinct from ionic diffusion) is provided by the behaviour of cells such as

0·1 KCl | 0·1 HCl | 0·1 KCl.

The chloride concentration is the same throughout the system. As the ionic concentrations must be almost the same with these two solutions, the layer formed by diffusion should have the same concentration gradient as that formed by mechanical mixing—yet such cells show large "time changes."

It is difficult to explain this in any other way than by assuming that salt migration takes place to a considerable extent.

Practical Application of the above Results.

To obtain accurate measurements of potential it is necessary to form a new boundary shortly before the measurement is taken, otherwise a serious error may be introduced.

It is desirable that the two solutions should be mechanically mixed at the boundary, and this is the more important the narrower the tube in which the boundary is formed.

Capillary tubes should be altogether avoided in the construction of an electromotive cell.

The electromotive force of any cell which derives part of its potential from the presence of a liquid contact is not constant, but varies with the time which has elapsed since formation of the boundary; if due attention is paid to the precautions mentioned above, consistent and comparable results may be obtained.

* *Loc. cit.*

ADDENDUM.

Note on the Use of Membranes.

There have been many investigations into the effect of membranes on potential, but, so far as we can find, no experiments have previously been made with elimination of the electrode potential by making the cell symmetrical, except for the membrane. The following measurements may therefore be of interest. The cells examined were of the type

$$\underset{a}{\text{1·0 KCl}} \mid \text{connecting solution} \mid \underset{b}{\text{1·0 KCl}},$$

where a membrane was interposed at the boundary *a* and the solutions were mechanically mixed at the boundary *b*. The two half-cells were connected

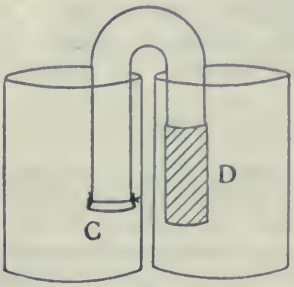


FIG. 5.

by means of a siphon (Fig. 5), which was closed at one end C by a membrane. To the other limb of the siphon was attached a rubber tube D. The siphon was filled with the connecting solution, inserted in place, and the solutions mixed at the open end of the siphon by compressing the rubber tube once or twice.

Various membranes were used with different connecting solutions. Table V gives the observed potential in millivolts, the sign referring to the electrode on the side of the membrane.

TABLE V.

Membrane.	Connecting Solution.		
	1·0 HCl.	1·0 NaOH.	1·0 LiCl.
Parchment	+3·1	−6·0	+0·6
	+3·2	−5·5	+0·0
			+0·6
Hardened filter-paper ...	+2·9	−1·5	0·0
	+2·3	−2·3	—
Cargile membrane	+2·5	−0·8	+4·5
Goldbeater's skin	+2·8	−2·3	0·0
Collodion on silk	+1·7	0·0	+0·5
Fine silk	nil	nil	nil

The values given were those obtained a few minutes after the cell was completed by insertion of the siphon. In most cases the potential fell steadily to zero, but in some cases the rate was very slow, *e.g.*, using a parchment membrane at the boundary (*a*), with the cell

$$1{\cdot}0\ \mathrm{KCl} \mid 0{\cdot}1\ \mathrm{HCl} \mid 1{\cdot}0\ \mathrm{KCl},$$
$$(a) \qquad (b)$$

the following values were obtained :

Time in minutes ...	0	4	10	25	40	55	75	105	120	(26 hrs.)
E.m.f.	(6·5)	2·5	3·5	2·5	2·5	2·6	2·8	2·8	2·8	1·3

The normal electrodes, before and after all such measurements, gave no potential when in direct connection.

Another set of values may be quoted, as they indicate the serious error likely to be introduced in actual practice if membranes or plugs of filter-paper are used. Using the apparatus as shown in Fig. 2, but with a tight plug of filter-paper in the end of the tube, it was found that an apparently steady potential was obtained with the cell

$$1{\cdot}0\ \mathrm{KCl} \mid 1{\cdot}0\ \mathrm{HCl} \mid 1{\cdot}0\ \mathrm{KCl},$$

the e.m.f. remaining constant at + 4·5 millivolts for 35 minutes, and in a second experiment falling from + 4·5 to 3·9 millivolts in two hours. On removing the plug the potential at once fell to zero.

CHEMISTRY DEPARTMENT,
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NOTE ON THE ELECTROLYTIC DETERMINATION OF COPPER IN SOLUTIONS CONTAINING NITRIC ACID.

By ELIZABETH GILCHRIST, B.Sc., and ALEXANDER CHARLES CUMMING, D.Sc.

(*A Paper read before the Faraday Society, Wednesday, May 7, 1913.*)

It is a matter of common experience that in the electrolytic determination of copper in solutions containing nitric acid it is impossible to deposit the last two or three milligrams under ordinary conditions. J. H. Stansbie* has shown that this is due to the presence of nitrous acid and that with a stationary electrode the accumulation of nitrous acid in the neighbourhood of the cathode causes dissolution of copper. "At first the current deposits the metal much faster than it is redissolved, but finally, when only traces of metal are present in the solution, dynamic equilibrium is attained, and no further permanent deposition of the metal can take place."

We might add to this statement that, with accumulation of nitrous acid in the solution, the rate of dissolution after some time often exceeds the rate of deposition.

Stansbie showed that with a rotating cathode satisfactory precipitation is obtained from solutions containing up to 3 grammes nitric acid per 100 c.c. of solution and that addition of sulphuric acid was advantageous.

It appeared likely from Stansbie's results that, if the nitrous acid was destroyed by means of urea, satisfactory results would be obtainable with stationary electrodes. As a preliminary test, a solution was electrolyzed which contained 0·508 gramme of copper and 10 c.c., of concentrated nitric acid, diluted to 100 c.c. The potential between the electrodes was 2·8 volts and the current was passed for two hours. It was found that 0·120 gramme of copper was undeposited.

To a second solution 5 grammes of urea were added, the quantities and conditions being in all other respects identical with those in the first experiment; in this case only 0·009 gramme of copper remained undeposited after the two hours' electrolysis.

The addition of urea evidently produced a marked improvement, but from these experiments alone the results could not be definitely ascribed to removal of the nitrous acid. In these experiments the voltage was kept constant but the current was not noted. In later experiments it was found that addition of urea raised the voltage between the electrodes (*i.e.*, lowered the conductivity of the solution) and caused a fall in the current. In all experiments deposition was much faster in presence of urea.

The following experiments confirm Stansbie's results as to the remarkable effect of nitrous acid in promoting the solution of copper by nitric acid and prove that the urea acts by removal of the nitrous acid. Thin sheets of

* *Trans. Faraday Soc.*, November, 1912.

electrolytic copper of equal size were placed in the various solutions for three hours and the loss in weight determined. In each case the quantities given are for 100 c.c., of solution ; 10 c.c. of ordinary concentrated nitric acid (sp. gr. 1·42) was added in each case and the solution diluted to 100 c.c. ; the amount of nitrous acid given is the amount present per 100 c.c. *before* addition of the urea.

No. of Experiment.	Nitrous Acid. Milligrammes.	Urea added. Grammes.	Weight of Copper dissolved. Milligrammes.
1	0·06	—	2·5
2	0·06	2	0·8
3	1·5	—	25
4	0·1	—	4·5
5	3	—	140
6	3	1	0·8
7	31	—	240
8	31	2	1·0

Experiments 7 and 8 illustrate in a marked manner the effect of urea. Experiments 2, 6 and 8 show that there is little danger of copper dissolving if urea is present. In the electrolysis experiments the presence of urea if therefore very advantageous in minimizing the risk of re-solution at the end of the experiment. If a little urea is added when deposition is complete, the current can be stopped and the vessel washed out without any re-solution of copper, provided that no unnecessary time is spent on the process. The consequent large dilution which results from the ordinary siphoning method of washing is thereby avoided.

A number of experiments were made to find the best conditions for complete deposition with stationary electrodes. The electrolyses were performed in a platinum basin with a perforated platinum disc as anode. If the current used exceeded 3 amperes the deposit was usually spotted. With a potential difference between the electrodes of 2·5 to 3 volts and a current not above 3 amperes, beautiful coherent deposits were obtained. If the current was continued for any considerable time after deposition was complete the deposit usually became spotted. The following results show that complete deposition can be obtained even when the solution contains 10 c.c. of concentrated nitric acid per 100 c.c. of solution.

Cu present = 0·5080 *gramme.*

1. 100 c.c. of solution containing 10 c.c. nitric acid and 5 grammes urea. Potential difference about 2·8 volts. Current passed for three hours. Cu found = 0·5090 gramme. Error + 1 mg.

2. 100 c.c. of solution containing 10 c.c. nitric acid. Current passed for two hours without urea ; then added 2 grammes urea and passed current again for one hour. Potential difference from 2·5 to 2·8 volts. Cu found = 0·5080 gramme. Error less than 1 mg.

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DISCUSSION.

Dr. V. H. Veley (*communicated*): The authors of this paper appear to be quite unaware of work published upon this subject, *Proc. Roy. Soc.*, 46, pp. 216–222, and more fully, *Phil. Trans.*, 182 (1891), pp. 279–317, in which it was shown that the apparent solution of copper in nitric acid is dependent upon the presence of nitrous acid. If substances as urea, hydrogen peroxide, the most effective agent, or other compounds are added to destroy the nitrous acid as fast as it is formed, then no solution of the metal takes place. As a consequence of this work the writer was accustomed, some twenty-five years ago, before the date of rotatory electrodes, to instruct students to add a few crystals of urea, or a few drops of hydrogen peroxide to complete the deposition of copper by the electrolytic process, if any nitric acid had been used to prepare the solution used for the determination. But it was not thought necessary to publish any comparative experiments, as such would follow as a necessary corollary of the investigations cited above.

The general results for copper apply equally to the metals silver and bismuth, as also to mercury, if an electrolytic determination of this last metal were considered desirable.

Dr. A. C. Cumming (*communicated*): I am sorry that Dr. Veley thinks we have not given him due credit for his valuable pioneer work in this field. The above note was intended solely to direct attention to a useful laboratory device, and it is of course merely an application of Dr. Veley's discoveries.

AN OXIDIZABLE VARIETY OF NITROGEN.

By T. MARTIN LOWRY, D.Sc.

(*Communicated to the* TRANSACTIONS *of the Faraday Society.*)

The photographs which are reproduced in the present Paper are of interest both from the spectroscopic and from the chemical point of view. On the spectroscopic side they represent an application of this method of investigation to gases which were so dilute that a column of gas 64 feet in length was required to produce an adequate absorption. On the chemical side they provide evidence, which appears to be unique, of the existence of an oxidizable modification of nitrogen, an allotropic form of the element which is perhaps the first essential product in its fixation. A brief summary of the conclusions arrived at has been published in the *Transactions* of the Chemical Society,* but the photographic evidence on which those conclusions were based is now reproduced for the first time as a contribution to a subject which has figured frequently in preceding volumes of the *Transactions* of the Faraday Society.

The gases under investigation were obtained by the action of the electric discharge on air. Two forms of discharge were used. First, the "silent" discharge in a large Andreoli ozoniser containing sheets and grids of aluminium, thirteen in number and 30" × 30" in area, separated by sheets of micanite. Second, a sparking discharge between a series of iron studs separated to a distance of $\frac{3}{32}$". Three groups of 6 spark-gaps and two of the Andreoli ozonisers were used at various times.

The chief interest of the work consisted in a comparison of the gases obtained from the ozoniser and spark-gaps separately with the "combined" gas obtained by using both forms of discharge, in accordance with a process devised by Mr. Sydney Leetham, of York, in 1903. At the time when the experiments were made the bleaching gases manufactured by this process were usually obtained by blowing air at the rate of about 70 c.f.m. through one of the ozonisers and then through a box in which 3 spark-gaps were energized in series with the ozoniser by an alternating current of 0·1 ampere at 9,000 volts. Other arrangements were, however, described, and some of these were tested by the spectroscopic method.

The *spectroscopic apparatus* consisted of three parts:

(1) A wooden *trunk* 64 feet in length and 3" × 3" in section, the volume being thus about 4 cubic feet. The trunk was provided with glass windows at each end, and inlet and outlet pipes were provided for the gases under examination. The effective length of the trunk could also be reduced to 16 feet by inserting a glass slide and using an additional "blow-off" hole so that the gas was confined to the earlier portion of the trunk.

(2) A *Nernst lamp* with filament vertical served as a source of light. It was placed in the focus of a condensing lens of 3¼" focal length, fixed

* *Trans.*, 1912, 101, 1152–58.

immediately in front of one of the glass windows. At the other end of the trunk the light was picked up again by a condensing lens of 11" focus, but on account of the great length of the trunk the image formed by the second lens was circular in form, all the light from the upper and lower portions of the filament being lost against the sides of the trunk, so that the effective illumination was derived only from a minute portion in the centre of the filament.

(3) The *spectroscope* was provided with achromatic quartz-calcite lenses of 13" focus, but when it was desired to photograph the spectrum a camera with a lens of 22" focus was used. Wratten and Wainwright's "panchromatic plates" were used with six minutes' exposure and two minutes' development in the dark.

The exposures shown in Plate 1 at once revealed the fact that, whilst the ozoniser and spark-gaps separately produced no visible absorption, the flutings characteristic of nitrogen peroxide could be recognized clearly in the spectrum which had been photographed through the "combined" gas. The copper spectrum shown at the bottom of the plate served for calibration, the two yellow and three green lines being clearly seen at one end and two violet lines at the other end of the spectrum.

In order to estimate the amount of nitrogen peroxide in the "combined" gas it was necessary to prepare a series of standard photographs. Some of these are shown in Plate 2, and indicate that the proportion of nitrogen peroxide in the "combined gas" is not far from $\frac{1}{10000}$ by volume. The standard photographs were taken with mixtures of nitric oxide and air, prepared with the help of the apparatus shown in Fig. 1. The nitric oxide was made from mercury and nitric acid ; its purity was tested by absorption with ferrous sulphate. It was collected in a cylinder funnel, provided with a T-piece and a capillary funnel through which mercury could be poured : the volume of mercury used in a given time afforded a measure of the volume of nitric oxide transferred to the "mixing jar." In this jar nitric oxide was diluted with known volumes of air run in from a standard meter. The mixture of nitric oxide and air was taken from the bottom of the mixing-jar and passed on to the trunk for observation.

Plate 3 reveals the remarkable fact that the proportion of nitrogen peroxide in the "combined" gas is but little affected by passing the air through the ozoniser and spark-gaps in the reverse order. Under these conditions the ozoniser alters its function completely and becomes a very efficient generator of nitrogen peroxide, producing this gas in larger quantities even than the series of 17 spark-gaps used for the last exposure on the plate.

Up to this point the efficiency of the "combined" arrangement appeared to be due to some alteration in the function of the spark-discharge when supplied with ozonised air, and of the silent discharge when supplied with sparked air. Plate 4 shows, however, that the problem is essentially chemical rather than electrical or electrochemical in character. The three exposures at the top of the plate show that almost equal yields of nitrogen peroxide are produced when part of the air is passed through the ozoniser only, and part through the spark-gaps only, the two products being afterwards mixed on the way to the trunk. In this arrangement a greatly increased yield of nitrogen peroxide is seen to result from the *chemical* interaction of two parallel currents of air after both have passed away from the electric discharge.

This result might be interpreted as meaning that the ozone produced by the silent discharge oxidizes to nitrogen peroxide some lower oxide of nitrogen produced by the spark-discharge. But this oxide could only be nitric oxide,

(*a*) Blank

(*b*) Ozoniser only.

(*c*) 3 Spark-gaps only.

(*d*) "Combined" gas.

(*e*) Copper arc.

PLATE I.

(*a*) "Combined" gas. 64 feet.

(*b*) "Combined" gas 15 feet.

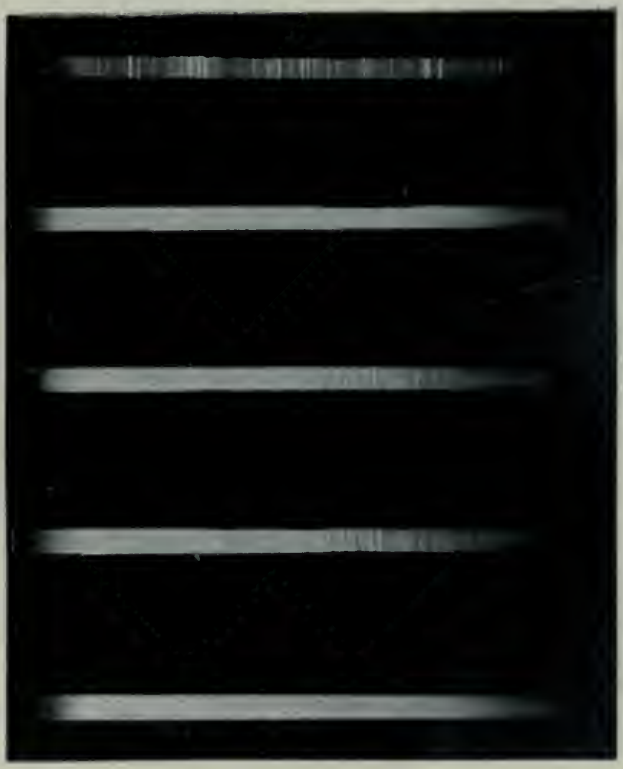
(*c*) NO_2 $\frac{1}{80}$.

(*d*) NO_2 $\frac{1}{2500}$.

(*e*) NO_2 $\frac{1}{5000}$.

(*f*) Copper arc.

PLATE 2.



(*a*) Copper arc.

(*b*) Blank.

(*c*) "Combined" gas (reversed arrangement) (3 spark-gaps ⟶ ozoniser).

(*d*) "Combined" gas (ordinary arrangement) (ozoniser ⟶ 3 spark-gaps).

(*e*) 17 Spark-gaps.

PLATE 3.

(*a*) "Combined" gas (½ c.f.m.) parallel arrangement (3 spark-gaps and ozoniser).

(*b*) "Combined" gas (½ c.f.m.) reversed arrangement (3 spark-gaps ⟵ ozoniser).

(*c*) "Combined" gas (½ c.f.m.) ordinary arrangement (ozoniser ⟶ 3 spark-gaps).

(*d*) 17 Spark-gaps (½ c.f.m.).

All the above gases were passed through the trunk at a slow rate (⅓ c.f.m. instead of 70 c.f.m.) to give time for the gases to mature.

PLATE 4.

as nitrous oxide is too unstable to be produced by sparking. The explanation would therefore amount to a suggestion that an insufficient time had been allowed for nitric oxide to be oxidized to nitrogen peroxide by atmospheric oxygen before the gas escaped from the trunk, unless the oxidation were accelerated by ozonising the air. That such an effect may exist is shown by the fact that, whilst the proportion of nitrogen peroxide present in the gas obtained from a series of 17 spark-gaps amounted to about $\frac{1}{7000}$ when the gas was passed rapidly through the trunk (Plate 3*e*), it was increased to about $\frac{1}{3000}$ (Plate 4*d*) when the velocity was reduced to $\frac{1}{2}$ c.f.m., by blowing off most of the gas, in order to allow ample time for the gas in the trunk to mature. But this explanation is not sufficient to account for the whole of the observations, since even under the very favourable conditions of the low-velocity experiments 17 spark-gaps were required to produce a yield of nitrogen peroxide only one-third greater than that obtained from 3 spark-gaps with the help of ozone.

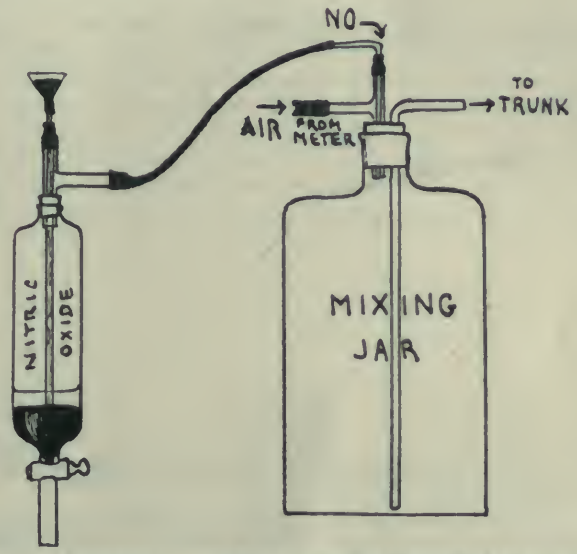


FIG. 1.—Apparatus for preparing Standard Mixtures of Nitric Oxide and Air.

The efficiency of the ozoniser must evidently be attributed to its ability to oxidize to nitrogen peroxide some substance which cannot be so oxidized by air. This oxidizable substance can scarcely be other than a variety of nitrogen itself, produced by the spark-discharge in much the same way that ozone is produced by the silent discharge. The most efficient way of oxidizing it is to produce it in an atmosphere already charged with ozone (Plate 4*c*). A rather less efficient method is to pass the air in which it is produced directly into an ozoniser (Plate 4*b*). Less efficient still is the arrangement whereby the oxidizable nitrogen is mixed with ozonised air in a mixing chamber a few feet away from the discharge apparatus (Plate 4*a*). The slight, but clearly marked gradation in the first three exposures of Plate 4 affords unmistakable evidence of the instability of the oxidizable variety of nitrogen, which appears to revert in the course of a few seconds to a form in which it can no longer be oxidized either by oxygen or by ozone.

The observations now described are probably of importance in connection with the technical fixation of nitrogen. It is not unreasonable to suggest

that, since the whole of the oxides of nitrogen must be produced by the union of disrupted molecules of nitrogen with disrupted molecules of oxygen, the most important feature of the process may be to generate the oxidizable variety of nitrogen and then to provide a supply of atomic or of ozonised oxygen to oxidize it before it reverts to the ordinary inactive form.

As a point of contrast it should be noticed that Strutt's chemically active nitrogen is not oxidizable by ozone under the conditions of his experiments.

The author is indebted to Mr. Henry Simon, of Manchester, for permission to publish an account of these experiments.

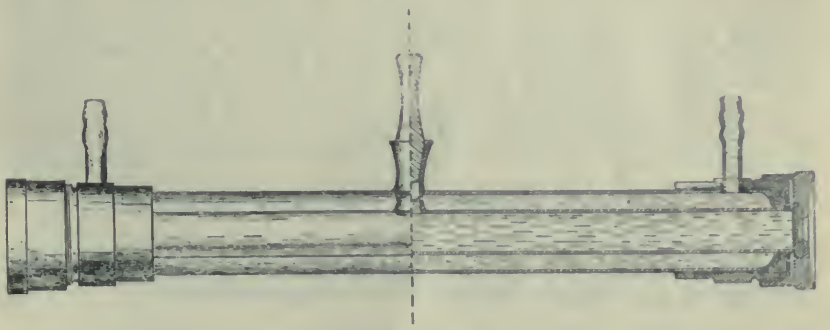
Full technical particulars of the electrical apparatus may be found in a paper read before the British Association at York entitled "The Electrical Discharge in Air," by W. Cramp and S. Leetham. An account of the effect of ozone on the fixation of nitrogen appears in a paper on "The Electrical Discharge," *Proc. I.E.E.*, 1908, p. 297.

A SILICA-JACKETED SILICA POLARIMETER TUBE.

By T. MARTIN LOWRY, D.Sc.

(*Communicated to the* TRANSACTIONS *of the Faraday Society.*)

In order to carry out experiments on the action of ultra-violet light in stimulating isomeric change * it was necessary to construct a silica polarimeter tube with a silica water-jacket. The tube shown in the figure was found (in contrast to an earlier design) to render admirable service, and is put on record as a successful solution of the problem. The chief feature of the design is that the silica jacket is actually fused on to the central tube, and that a fused joint is also made at the point where the funnel-shaped aperture of the central tube passes through the water-jacket. The metal ends of an ordinary polari-



meter tube are slotted to admit the silica side-tubes through which the water enters and leaves the jacket, and are cemented on to the silica parts of the apparatus. The silica discs which close the ends of the polarimeter tube can then be screwed tight in the usual way.

Silica polarimeter tubes are difficult to keep clean. If the tube becomes contaminated with traces of alkaline impurities it seems to be impossible to clean it by washing or soaking, and the catalytic action of the wall of the tube often becomes far worse than in the case of a glass tube. In the present case this difficulty was overcome by removing the metal parts of the tube and igniting the silica.

The "end-on" mercury lamp described in these *Transactions*,† placed alongside the polarimeter tube, provided an excellent source of powerful ultra-violet light.

* *Trans. Chem. Soc.*, 1913, **103**, 1214–1221.

† *Trans.*, 1912, **7**, 267–270.

REVIEWS OF BOOKS.

The Principles of Applied Electrochemistry. By A. J. Allmand, D.Sc. (London, 1912 : Edward Arnold. Pp. xii + 547, with 136 illustrations. Price 18s. net.)

The character of Dr. Allmand's book is indicated accurately in the title. The first part of the book, covering 192 pages, deals with general questions, whilst the "Special and Technical" chapters form the second part. In the first part are included chapters on the fundamental laws of electrolysis, together with such general subjects as Osmotic Pressure, Equilibrium, Power, and Energy; the concluding chapter contains a very valuable account of Electrical Discharges in Gases, in which characteristic curves are given showing the remarkable variations of voltage which take place as the type of discharge alters with increasing current. The second part deals with all the main applications of electrochemistry, Batteries, Copper Refining, Alkali and Bleach, Aluminium, Electric Steel, Carbides and Nitrogen-fixation, together with a great many of the minor electrotechnical products. These are described concisely, with diagrammatic illustrations, but without attempting to give complete details or working costs. This renders the book sufficiently concise to enable a student or beginner to obtain a good general idea of the present position of technical electrochemistry, which can afterwards be supplemented by reading the papers and monographs in which the different processes are fully described. It will also be of great value to many teachers and others who are not specialists in this field but wish to obtain reliable information as to what is actually being done at the present time in applying electrical power to the preparation of chemical products. The book can be heartily commended to all who are interested in this important problem.

Monographs on Inorganic and Physical Chemistry. Per-acids and their Salts. By Dr. T. Slater Price. (London, 1912: Longmans, Green and Co. Pp. 123. Price 3s. net.)

For many years past it has been customary to publish monographs on various branches of chemistry in preference to great tomes of a general character. To those who wish to study any particular subject the monographs are of the utmost value. The student obtains the whole of the information for which he is seeking collected together and is thus saved an enormous amount of research through the general literature.

It is of course of the greatest importance that those who undertake the writing of these monographs should know their subject well, should know what to include and what to exclude. By this we mean that nothing essential should be left out, but that discretion should be used so that the monograph does not become unwieldy. Judged by these standards the book before us is excellent and will be found of great value to those who wish to study the properties and reactions of the per-acids and their salts and their modes of preparation.

The book commences with an introduction giving a general résumé of what constitutes the per-acids and their place in the periodic law of the elements which will form per-acids. As persulphuric acid and persulphates have been worked at more than other per-compounds, and furthermore persulphuric acid was the first to be prepared, it is natural that a large amount of space should be given to their consideration.

It is not necessary to go through the contents of the book, but simply to say that the book is well written and very useful and brings the subject up to date.

Monographien ueber Chemisch-technische Fabrikations-Methoden. Band XXIV : Anwendung physikalisch-chemischer Theorien auf technische Prozesse und Fabrikationsmethoden. By Prof. Dr. Robert Kremann. (Halle, 1911 : Wilhelm Knapp. Price 9.50 Marks.)

The extraordinary strides which physical chemistry has made within the last twenty years are probably greater than the advancements made in any other branch of chemistry. For some time physical chemistry and physical chemists were rather looked at askance by technical chemists. Possibly the physical chemist was to some extent to blame, because at one time he showed a tendency to talk too much in terms of the new branch, which sounded to many people pedantic. Thus, those who had been accustomed to talk of an acid did not like the term hydrogen ions to explain acidity. By degrees, however, physical chemistry is taking its place in the technical world and many reactions which before were obscure are being elucidated. Take for example the manufacture of hypochlorites and chlorates electrolytically. The two processes have been most carefully worked out from the physico-chemical side, but until this was done the success of the processes was very limited. If anything seemed theoretical and unpractical it was colloidal chemistry, and yet now we find it entering into all sorts of processes a few years ago absolutely undreamed of. Physical chemistry has been of the utmost value, too, in catalytical processes.

In the book before us we find such subjects as the following dealt with. The two chief laws of the mechanical heat theory, Speed of Reaction and Katalysis, Effect of Temperature on Rate of Reaction, Employment of Phase Rule, The Employment of the Phase Rule in Fluid and Solid Solution, The Theory of Colour, The Theory of Vulcanisation, Soap Manufacture, The Ammonia Soda Process, and so on. In fact the book covers almost all branches of chemical technology.

The book is well written and will be found very useful as illustrating the importance of carefully worked-out theories to the practice of chemical technology.

Analytische Schnellmethoden. By Dr. Victor Samter. (Halle, 1912 : Wilhelm Knapp. Pp. 237. Price 10 Marks net.)

The proof of the usefulness of a book on practical chemistry is the employment of it in the laboratory and the deductions one is able to draw from its use. There is, from the author's point of view, one drawback in connection with this, and that is, if it is the reviewer who is thus testing its merits he may have to wait some time before a notice is published. The reviewer therefore desires, in the first place, to apologize to the author and publisher for not having written the notice at an earlier date.

The book has been used in the reviewer's laboratory for more than twelve months and it has taken a most useful position there; in fact it has become

almost indispensable. It is of enormous advantage to have an account of rapid and accurate methods of analysis brought together in one book. Processes from all parts of the book have been used, and with one or two exceptions—where the description of the method has not been quite full enough—excellent results have been obtained.

It is not necessary in a review to describe the methods contained in a book on analysis, except to state that all the ordinary metals and metalloids are given. There is a short introduction descriptive of methods; for example, Electro-analysis, Titration, Gas Analysis, Specific Gravities, the Use of the Refractometer, and so on.

Having, as already stated, used the book, we most heartily recommend it, and think it ought to be found in every laboratory, particularly in technical laboratories.

Practical Measurements in Radioactivity. By W. MAKOWER, M.A., D.Sc., and H. GEIGER, Ph.D. (London, 1912: Longmans, Green & Co. Pp. x + 151. Price 5s. net.)

Apart from those who are doing original work, very few students acquire a first-hand knowledge of radioactivity. In the University of Manchester, however, such measurements form a regular part of the practical work in the Honours School of Physics. These experiments and others designed for the training of those wishing to undertake original work are described in the volume now under review. After an account has been given of the radiant electrometer and a variety of electroscopes, measurements of the α, β, and γ rays are described. Subsequent chapters deal with the active deposits and radioactive recoil, radioactive transformations, standard measurements, and the separation of radioactive substances. The subject is presented in a very attractive form, and it would be difficult to imagine a book which would be better suited to carry out the purpose which the authors have in view.

Monographien ueber Chemisch-technische Fabrikations-Methoden. Band XXII: Die Zeresinfabrikation. Von Dr. BÉLA LACH. (Halle, 1911: Wilhelm Knapp. Pp. 207. Price 9.60 Marks net.)

The manufacture of candles and other articles from solid paraffin, ozokerite, and so on is of enormous importance. Strangely enough, although we now have lighting by incandescent methods and electric lighting, yet the manufacture of candles is continually increasing. Enormous quantities of candles are used in India and China, and in Africa. It is therefore very interesting to have a monograph on the subject.

In the olden days, tallow candles made from mutton and beef fat were the chief means of illumination. There were also the lamps in which whale oil and other animal oils were used. We have not, indeed, to go very far back to remember the oil lamps of the railway carriages, the oil of which was chiefly obtained from the whale. In some parts of the world, notably in Galicia, on digging down to certain depths plastic masses of semi-solid paraffin are found. When first discovered this product was supposed to be of no value. After a time, however, it was discovered that this material could be used as a source of illumination. In 1862 it was found that light petroleum and solid wax could be obtained by distillation of this earthwax. Dr. Letheby, of Field's Candle Works, in London, was the first to prepare paraffin wax in this manner.

The book before us, which deals with the production and working up of these products, is divided into two parts. The first part deals with the

occurrence and working up of the product. In the first chapter, after discussing the occurrence of this earth wax, its geological formation is considered, and then the physical and chemical properties of the material. We then come to the methods of obtaining the ozokerite. By the old methods shafts from 30 to 50 metres were sunk, and the material was sent up mixed with earthy matter by means of buckets. To-day the pits are often sunk to a depth of 250 metres. This has been made possible by improved means of ventilation and because of improved pumps to remove the water which collects in the mines. The method of washing and melting the wax is described. Methods of analysis to prove the purity of the product are then discussed.

The second part of the book deals with the manufacture of ceresin from the crude product and the various methods adopted. This part of the book is well illustrated by excellent line drawings showing the plant and machinery employed. What we like about the book is that it is written entirely from the technical standpoint, and it will therefore be of the greatest value to the technical worker. It is written in a broad-minded way, and will be of use not only to those who are engaged in this particular industry, but to those in allied industries. In the designing of plant the designer can frequently, almost invariably, adapt methods and processes from what, at the first glance, would appear to be machinery only adapted to one particular industry.

We always receive these monographs with pleasure, but this particular monograph is deserving of special commendation, and we heartily congratulate the author and the publishers who are bringing out this series.

Tables Annuelles Internationales de Constantes et Données Numerique. Vol. II. Année 1911. (London, 1913: J. & A. Churchill. Pp. xl + 760. Price, paper, 25s. 6d.; cloth, 28s. 6d.)

It was anticipated that greater activity on the part of the Editor would have resulted in some diminution of bulk in the Annual Tables for 1911, as compared with those for the preceding year. This anticipation has been disappointed, as there is an increase of 32 pages to be recorded. The production annually of a volume of 800 pages has already overtaxed the resources of the International Commission by which the tables are produced, and cannot but produce a similar strain on the purses as well as on the bookshelves of the subscribers. If the enterprise is to survive and prosper, drastic action on the part of those responsible is urgently called for. In the present volume one of the most conspicuous cases is found in the fact that not less than 15 large pages are devoted to reproducing data from an easily accessible paper by Du Bois and Elias on the "Influence of Temperature and of the Magnetic Field on Absorption and Phosphorescence Spectra," 13 pages being given to the action of the magnetic field in the case of crystals of erbium nitrate! The number of workers who would need to consult these data in detail cannot be more than half a dozen, and these would almost certainly be the possessors of reprints of the original paper. It cannot, therefore, be contended that any useful purpose has been served by devoting page after page of the tables, and a sum of money which can scarcely be less than £50, to the production of a reprint which must necessarily be less reliable and less authoritative than the original. The value of the tables depends very largely on the efforts that have been made, with marked success, to classify the scattered data which are to be found in inaccessible papers or in papers whose titles do not indicate clearly the presence of numerical data. It would be a sound rule if every case in which it is proposed that more than one page

of the tables should be devoted to a single paper were submitted to the permanent Commission, who would decide whether reproduction *in extenso* was justified by the inaccessibility of the paper or by its wide general interest.

Apart from this question of policy the preparation of the tables has been very well done. One English author will be puzzled to recognize himself as Th.-P. Hilditsch ; this curious custom of putting a hyphen between the initials of two christian names has been adopted throughout, but is not sufficiently universal to justify its adoption in a set of international tables. The Russification of the name is a misprint of a kind that is rare in the present volume.

As regards the printing of the tables, waste of space is not so obvious as before, but in the section on solubility one-third of several pages is devoted to printing "dans 100 g. d'eau" or "dans 100 g. de la solution" over and over again, reducing the matter to two columns in a page where it would have been easy to print three.

Osmotic Pressure. By Professor A. FINDLAY, M.A., D.Sc., F.I.C. (1913 : Longmans, Green & Co. Pp. iv + 84 (with 2 figures). Price 2s. 6d. net.)

Professor Findlay's monograph on "Osmotic Pressure" is an expansion of his recent admirable article in "Scientia." It contains a summary of the experimental work of the Earl of Berkeley and of Morse and Fraser, and a discussion of their data in the light of G. N. Lewis's theory of the Ideal Solution. It can be heartily commended to all who are interested in the subject.

A Laboratory Manual of Alternating Currents. By JOHN H. MORECRAFT. (London, 1912 : Longmans, Green & Co. Pp. 247. Price 7s. 6d. net.)

This book comprises 39 sets of experiments and is addressed to those who already have a considerable knowledge of the subject. Like many other text-books of American origin, it shows a good and vigorous departure from traditional lines—it is no mere collection of diagrams of connections with column-headings for observations. The directions for each experiment are preceded by a theoretical disquisition on the matter in hand, and it is in these theoretical parts that the great value of the book is found. We believe that in England the purpose of the book, viz., use as a laboratory handbook, will only be possible in first-class laboratories, well equipped both in apparatus and staff ; but in view of its title it must be pointed out that the work should be of great assistance to any advanced student as a compendium of alternating-current theory, quite apart from the laboratory or test-room. Indeed, it is good to find within the compass of one book the treatment of so many matters which even to the reader of good acquirements are too often inaccessibly buried in the advanced mathematical treatises of the subject.

Emphasis is laid upon the correct interpretation of instrument reading ; armature reaction and the parallel running of generators and transformers are well handled ; and the relationships for polyphase power generation and transformation are clearly set forth. The inclusion of readable chapters on the variable speed induction motor, the interpole converter, and the induction generator is a particularly good feature. A series of oscillograph and ondograph records is included as an appendix, and these, although poor as process work in several instances, give a marked sense of reality to many of the points raised in the text.

Monographien ueber Chemisch-technische Fabrikations-Methoden. Band XXIII: Die Darstellung von Bisulfiten und Sulfiten. By Dr. E. Schütz. (Halle, 1911: Wilhelm Knapp. Pp. 64. Price 2.80 Marks net.)

Although of great importance commercially, the production of bisulphites has not been described in much detail in works on Chemical Technology. Therefore the monograph of Dr. Schütz, which brings the subject together in a compact form, will be found of great value to those who desire to study the subject.

In the first place the author describes the various methods of producing sulphurous acid. On the small scale sulphur is usually the starting-point for the preparation of the gas, but in large works iron pyrites, copper pyrites, or zinc blende are usually roasted. The various forms of retorts and furnaces used in the preparation are described in detail.

As it is important the gas should be pure, a short chapter on purification methods is given. We then come to the production of the acid and neutral salts of sulphurous acids, that is to say, bisulphites. The first substance dealt with is sodium bisulphite, then normal sulphite, sodium pyrosulphite, the potassium salts, calcium salts, etc.

The last section deals with the uses of sulphites and bisulphites.

The monograph can be heartily recommended to those interested in the subject, and will be found a useful addition to all technical libraries.

La Télégraphie et la Téléphonie Simultanées et la Téléphonie Multiple. From the German of K. Berger, translated by P. le Normand. (Paris, 1913: Gauthier-Villars. Pp. 134. Illustrated.)

This book is a translation into French of K. Berger's "Gleichzeitige Telegraphieren und Fernsprechen und das Hehrfachfernsprechen," and deals with a subject which in this country has not received the attention which it deserves. The treatment of the subject is divided into three parts. The first, relating to the problem of telephoning on telegraph lines using an earth return, describes in detail the solution of van Rysselbergh and outlines the arrangements of Perego and Turchi-Bruné. Various arrangements of apparatus for telegraphing over metallic telephone circuits, including those of Picard and Dejongh, are described in the second part of the book, and the third part relates to systems of multiple telephony using "phantom" circuits. The ideas underlying the arrangements are described clearly from an elementary standpoint. In some cases the description is amplified by details of the apparatus usually employed by the Imperial German Telegraph Service, and some information is given as to subsidiary arrangements for testing the lines and preventing induction from exterior circuits.

Treatise on General and Industrial Inorganic Chemistry. By Dr. Ettore Molinari. Translated by Dr. Ernest Feilmann. (London, 1912: J. & A. Churchill. Pp. xvi + 704. Price 21s. net.)

This, the first volume of Molinari's imposing work, is a translation from the third edition of the Italian original, and its appearance will be heartily welcomed, not so much by the working chemist who in this age of specialization has perhaps little need for a general treatise, but by every teacher and every student of chemical technology, for whom the science means not merely generalized statements about the properties of matter, but also an understanding of the innumerable highly organized and complex processes which go to make up the material fabric of our modern civilization. The

book thus fills a real need, the complete linking together of theory and practice, and it will be appreciated accordingly. The general plan of the book is much like that usually adopted in works on chemistry, namely: a general introduction to the science, sketching its history and outlining its principal laws (pp. 1–125), and then divisions on non-metals (pp. 126–407) and metals (pp. 408–661), but in every section of Parts II and III immediate and constant reference is made to industrial methods and industrial applications, even to the extent of indicating commercial prices of chemical products; for are not these determining factors in the industrial struggle for existence?—and as far as we have been enabled to test the descriptions and the information, they are at once accurate, up to date, and on the whole given with a due sense of proportion, and we may add of style and interest, for the book is admirably written and, judging from the English text alone, admirably translated.

The sections on metallurgy are very much briefer than the other portions of the book, but in view of the excellent literature already in existence, this perhaps is no drawback. Some portions of the latter part of the book are, however, decidedly flimsy. Hardly a word is said, for example, on so interesting and important a subject as the electrolytic refining of copper; and the short section on photography, a subject which involves so many aspects of modern chemistry, might with advantage have been considerably expanded. There is a good index, but the references, excepting to patents, are very scanty.

Treatise on General and Industrial Organic Chemistry. By Dr. Ettore Molinari. Translated by T. H. Pope. (London, 1913: J. & A. Churchill. Pp. xx + 770. Price 24s. net.)

The publication of the second volume of Molinari's chemistry again brings before us the question of the consideration of technology in the study of chemistry. Hitherto organic chemists, unlike inorganic chemists, have carefully avoided giving more than very scanty details of technical processes in the ordinary text-books. This may be due to the great difficulty of including in a book of comparatively small dimensions anything more than a brief summary of the rapidly growing knowledge of pure organic chemistry. Dr. Molinari seems to have solved this difficulty in an admirable manner, although one cannot help thinking that he overrates the importance of the technical side of organic chemistry to those students intending to become teachers. For those students taking up industrial chemistry as a profession the book provides an excellent text-book and a guide to more specialized treatises. On the whole the matter is well proportioned, but on the technical side full enough justice is by no means done to rubber and its substitutes. Moreover, very little is said of the uses of acetoacetic ester, while no mention at all is made of that reaction, which has so wide and varied an application and which was introduced by Friedel and Crafts. The treatise covers a very wide range, dealing in an equally interesting manner with such subjects as the origin of life and the details of the cultivation of certain vegetables, etc. One cannot, however, help being surprised at the entire absence of electrolytic methods in the manufacture of those organic bodies of commercial interest to which reference is made. The illustrations which have been liberally scattered throughout the book convey excellent impressions of the numerous kinds of machinery employed, and although too much use is made of a type so minute as to cause difficulty in reading, in other respects the book is very well printed. It only remains to add that mistakes are few and are mainly confined to printers' errors.

Electroplating. A Treatise on the Electrodeposition of Metals, with a Chapter on Metal-Colouring and Bronzing. By WILLIAM R. BARCLAY, A.M.I.E.E., and CECIL H. HAINSWORTH, A.M.I.E.E. (London, 1912: Edward Arnold. Pp. viii + 399. Price 7s. 6d. net.)

Rule-of-thumb methods seem to have taken possession of the art of electroplating more fully perhaps than obtains in any other branch of applied science. The purpose of this handbook is to give to the modern practical electroplater an account of his craft built up on a scientific basis, so that he may become a "scientific student" as well as a mere "practical man." The book is quite a good one of its kind. It is evident that the authors have intimate knowledge of all the thousand-and-one intricate little details that are involved in the apparently simple processes of the electrodeposition of metals, and they tell us that the various formulæ and directions recommended are all based on actual workshop practice and not on bare laboratory experiments. Whether, however, any text-book is capable of making an electroplater, who has not had the scientific fundamentals drilled into him at a very early stage in his career, work his baths scientifically is a proposition which our personal experience leads us very seriously to doubt. To be sure, we have here some introductory chapters stating very clearly the basic chemical, electrical, and electrochemical principles on which the art of plating is based, but frankly, we do not for one moment believe that a man can really be given to understand ever such a simple generalization of Ohm's Law merely by reading an account of it, be it ever so lucidly put. It is for this reason that we regard the introductory chapters in manuals of this kind, amounting in the present case to nearly one half of the book, as so much wasted effort. The student will either know the fundamentals before he becomes an electroplater, or else he will never know them at all, at least without going through the mill of a proper laboratory and lecture training; in either case the short treatment possible in the space available is superfluous. We are sure that a man who knew no more chemistry beyond what he gathered from the first part of this book would have not the haziest understanding of, say, the complex reactions described in the very excellent chapter on the deposition of nickel. Having said so much, however, it is all the more pleasurable to point out that the book contains in the small compass of the second half a very great deal of information that the electroplater—whether scientific or not—will find of the greatest possible use. The account given of methods of depositing the various metals is in many respects on much the same lines as in Mr. S. Field's well-known useful little text-book, but the present authors go into somewhat fuller detail, particularly in their discussions of methods of preparing the chemicals used in plating and of the compositions of the baths and the changes that take place in them in course of use.

Storage Batteries. The Chemistry and Physics of the Lead Accumulator. By HARRY W. MORSE, Ph.D. (New York, 1912: The Macmillan Company. Pp. 266. Price 6s. 6d. net.)

This little work on the theory of accumulators by the Assistant-Professor of Physics in Harvard University is quite the best of its kind that we know of. It is good because it is well written and concise; it does not attempt too much, but what it does set out to explain it admirably succeeds in making as clear and convincing as the most critical reader would desire.

The author develops his treatment of the subject in simple, straightforward fashion. An introductory and historical section is followed by an exposition

of the fundamental electrochemical laws and of the theory of ions, and then follows a very lucid account of the cell reactions based on the double sulphate theory and pictured in terms of ions. A consideration of the energy changes in the cell leads up to a more detailed analysis of the separate reactions at each electrode during both charge and discharge. The factors that govern capacity, efficiency, and internal resistance are next discussed in some detail, and then follow some chapters on the rather more concrete subjects of plate formation and construction, and, what, alas! is equally important, the troubles and diseases that plates are heir to. It will be seen that the author confines himself almost entirely to general principles without confusing the issues by reference to the myriad-type plates that have been conceived, constructed, and used—or scrapped. We think he is wise in his restraint, for a student who has made his own the principles expounded in this little volume should, with the necessary experience, have not the slightest difficulty in appraising at their true value the various types of battery plates that are set before the consumer's choice for whatever particular purpose an accumulator may be required.

Dictionary of Applied Chemistry. Edited by Sir Edward Thorpe, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition in Five Volumes. Vol. III., Gr–Oils. Pp. 789. Vol. IV., Oilstone to Soda Nitre. Pp. 727. (London, 1912 and 1913: Longmans, Green and Co. Price 45s. net each volume.)

Since the last issue of Transactions a further two volumes of the great Dictionary have appeared, with commendable regularity, and now but one remains to complete the work. There is little to add to what has already been said about the Dictionary, and needless to say the standard of the later volumes is in every way equal to that of their predecessors. Some of the articles, crowded as they are with data and information, are simply models of compression; such, for instance, as those on Naphthalene, Oils and Fats, and Resins. Others again give so well-considered and impartial an account of the present position of their subjects that they must prove to be simply invaluable to the busy man who wants to put his finger at a moment's notice on accurate and authoritative information and references. The articles on Metallography, Utilization of Atmospheric Nitrogen, Photography, Radioactivity, are examples picked at random from a score that might be mentioned for their excellences in these respects. As a time-saving appliance the Dictionary is simply indispensable.

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A GENERAL DISCUSSION ON THE PASSIVITY OF METALS.

At the meeting of the Faraday Society held on Wednesday, November 12, 1913, at the Chemical Society, Burlington House, London, W., a **General Discussion** on **The Passivity of Metals** took place. **Professor F. G. Donnan, F.R.S.**, was in the chair.

Specimens of non-corrodible steels and other ferro-alloys were exhibited by Sir Robert Hadfield (described by Mr. S. A. Main), Dr. J. Newton Friend, Mr. Robert Lennox, and Mr. John Evans.

INTRODUCTION

Dr. G. Senter opened the Discussion with a short résumé of the various theories of passivity which have found acceptance at different times.

The phenomenon of passivity was discovered by Keir * as far back as 1790. He observed that iron, after treatment with concentrated nitric acid, had lost the property of precipitating silver from solutions of silver salts, and was no longer attacked by dilute nitric acid. The name "passivity" we owe to Schönbein,† who made many important contributions to our knowledge of the subject. Faraday's name is also closely associated with the early history of this subject in connection with his well-known suggestion ‡ that passivity is due to the formation of a coating of oxide on the surface of the metal—an explanation which still has its supporters. For a number of years after 1840 our knowledge of passivity made comparatively little progress, but about fifteen years ago a new era of rapid advance set in. This stage was initiated by the classical experimental investigations of Hittorf,§ who worked

* *Phil. Trans.*, 1790, **80**, 359.
† *Pogg. Ann.*, 1836, **37**, 390 ; **38**, 444 ; **39**, 342 ; 1837, **41**, 53 ; 1838, **43**, 103.
‡ *Phil. Mag.*, 1836, 9, 53.
§ *Zeitsch. physikal. Chem.*, 1898, **25**, 729 ; 1899, **30**, 48 ; 1900, **34**, 385.

chiefly with chromium. Among recent investigators the names of Le Blanc, Foerster, Haber, G. C. Schmidt, and their co-workers deserve special mention. The predominant share which our German colleagues have taken in the recent developments of this subject is reflected in the number of papers which they have been good enough to contribute to our proceedings this evening.

As a general rule, progress in our knowledge of any particular subject is most rapid when there is considerable divergence of opinion with regard to the interpretation of the experimental results. Such divergence of opinion has been particularly marked in connection with passivity, and even at the present time three entirely different "explanations" of the phenomenon have their supporters. The controversy has now, however, reached such a stage that a considerable measure of agreement has been reached on many points and it is hoped that the open discussion of the subject arranged by this Society, by emphasizing points of agreement as well as points of difference, may indicate the most fruitful directions for further experimental investigation, and thus contribute in no small degree to progress in a very interesting and important subject.

History of the Subject.

Keir was led to the discovery of passivity by following out an observation of Bergman that some samples of iron are capable, others incapable, of displacing silver from its salts. One of Keir's most important observations may fittingly be described in his own words: "I digested a piece of fine silver in pure and pale nitrous [nitric] acid, and while the dissolution was going on and before the saturation was completed I poured a portion of the solution upon pieces of clean and newly scraped iron wire into a wine-glass and observed a sudden and copious precipitation of silver. The precipitate was at first black, then it assumed the appearance of silver, and was five to six times larger in diameter than the piece of iron wire which it enveloped. The action of the acid on the iron continued some little time and then it ceased, the silver redissolved, the liquor became clear, and the iron remained bright and undisturbed in the solution at the bottom of the wine-glass, where it continued during several weeks without suffering any change or effecting any precipitation of the silver."

Further experiments showed that the liquid had not lost its power of acting on *fresh* iron, although it had ceased to act on the piece exposed to it, so that the change was in the iron and not in the liquid. This led to the discovery that concentrated nitric acid alone renders iron passive, and it was further found that a sample of inactive iron regained its activity by rubbing it at a point or by bringing it in contact with a piece of active metal. The further remarkable observation was made that when a piece of active metal was placed in acid in which a piece of passive metal was lying, so that the two pieces did not touch, in a short time the passive metal became active. Keir, at the end of his paper, expresses his intention of returning to the subject in later communications, but this promise remained unfulfilled.

The next important contributor to this subject was Schönbein.* Space will only admit of a brief reference to two of his observations. In a letter to Faraday he points out that a piece of iron could be rendered passive by heating one end of it in an alcohol flame for a moment or two—not only the heated portion but the remainder of the wire is rendered passive. Further, other wires placed in contact with the partially oxidized wire are not affected in nitric acid of density 1·35 provided the oxidized end is first dipped in the acid; under ordinary conditions the wires dissolve readily in acid of this

* *Loc. cit.*

density. Later investigations* appear to show that portions of wire in contact with the heated portion are not passive, but can be passivated more readily than ordinary iron. The contradictory results obtained with nitric acid are probably to be accounted for by the observation that under certain conditions a relatively dilute acid (D = 1·250) can render iron passive.†

Schönbein was one of the earliest to investigate passivity by electrochemical methods, and he made the important discovery that iron could be rendered passive by making it an anode. in a cell in which oxygen acids were subjected to electrolysis (so-called "anodic polarization") Schönbein did not himself suggest any explanation of passivity, but raised objections to the oxide theory when it was put forward by Faraday. The reasons given by Faraday in favour of his theory are as follows:

(1) All known passivity phenomena are oxidation processes.
(2) Iron coated with oxide is insoluble in acids.
(3) The passive condition readily disappears on polishing the metal.

His words are as follows‡: "The iron is, in fact, as if it had no attraction for oxygen, and therefore could not act on the electrolyte present, and consequently could produce no current. My strong impression is that the surface of the iron is oxidized or the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation."

Schönbein urged, among other objections to Faraday's theory, that iron rendered passive in acids showed no trace of a coating of oxide. To this Faraday answered that he could find no better explanation, and that he would not maintain that the coating consisted of one of the known oxides, but resembled more a condition of very fine equilibrium.

As already mentioned, Faraday's explanation of passivity was pretty generally accepted up to the commencement of Hittorf's investigations in 1898. The bearing of these important investigations on the nature of passivity is dealt with below. Hittorf pointed out many serious objections to the oxide theory, but did not himself put forward any very definite explanation of passivity phenomena. In connection with his observation that active chromium dissolves in the divalent form whilst passive chromium dissolves at a much more higher potential with formation of compounds containing sexavalent chromium, it has been suggested that the passive form of a metal is a different allotropic modification, much "nobler" than the active form (see below).

A third theory of passivity, the so-called "reaction velocity theory," was put forward by Le Blanc§ in 1900, and has exercised a profound influence on the recent development of the subject. These three theories of passivity are discussed, and the arguments for and against them briefly stated in the next section.

Theories of Passivity.

The more important phenomena which have to be accounted for on any theory of passivity are as follows. The passive state is best known in connection with iron, cobalt, and nickel, but most, if not all the metals may be

* Hittorf, *Zeitsch. physikal. Chem.*, 1900, **34**, 395; Heathcote, ibid., 1901, **37**, 368.
† Heathcote *loc. cit.*
‡ Cf. *Experimental Researches*, "Everyman's Library" edition, p. 326.
§ *Zeitsch. Elektrochem.*, 1900, **6**, 472; 1905, **11**, 9; *Boltzmann Festschrift*, 1904, 183.

made to assume this state under suitable conditions. Passivity may be induced by immersing the metal in an oxidizing agent such as nitric or chromic acid, and in solutions of alkali hydroxides; also by anodic polarization in a great variety of electrolytes. When the force producing passivity is removed the metal as a rule returns to the active state, slowly at first and then more rapidly, in some cases almost instantaneously. When the surface of a metal in the passive condition is scratched or rubbed, it regains its activity at once. Treatment with acids, cathodic polarization with hydrogen, and raising the temperature all favour return to the active condition. A metal becomes much more positive (more "noble") when it changes from the active to the passive condition, and does not dissolve when the equilibrium potential is reached. On further increasing the anodic potential the metal may dissolve as a more highly oxidizing ion (*e.g.*, chromium), or the current may be employed mainly or entirely in discharging anions. The rise of potential on anodic polarization is usually slow at first, and then there is a sudden rise of considerable amount, the metal becoming almost insoluble. The nature of the anion has considerable influence. Thus the ions of oxidizing acids, such as NO_3 and ClO_3' favour passivity, whilst Cl' and Br' have the contrary effect. Other phenomena met with in this connection will be mentioned in the course of the discussion of the different theories of passivity.

As already mentioned, three theories of passivity have obtained a greater or less degree of recognition:

(1) The oxide-film theory of Faraday, already referred to.

(2) The valency theory of Krüger-Finkelstein* and W. J. Müller†; according to this theory passivity phenomena are due to the change of a metal to a "nobler" modification.

(3) The reaction velocity theory of LeBlanc.‡ In its most general form this theory states that passivity phenomena are due to slow rate of change (electrochemical or purely chemical) at the anode. In this form the reaction velocity theory is little more than a statement of the facts, and several special hypotheses have been put forward as regards the mechanism of the retardation. Thus we have—

(*a*) *The oxygen charge hypothesis* of Fredenhagen§ and Muthmann and Frauenberger.|| The cause of passivity is to be sought in the slow rate of reaction between the anode and the oxygen liberated there, with the result that the anode becomes charged with the gas, or, alternatively, a metal-oxygen alloy is formed.

(*b*) *The anion discharge hypothesis*, according to which the main change at the anode is not the formation of metal ions but the discharge of anions; the slow reaction of the discharged anions with the metal produces passivity. The views of Sackur (see below) are based on the assumption of a primary anion discharge.

(*c*) *The hydrogen activation hypothesis* of Foerster¶ and of Schmidt,** according to which the normal condition of iron is passive and it only becomes active under the influence of a catalyst. According to Foerster the catalyst is hydrogen; according to Grave,** a pupil of Schmidt, it is hydrogen ions.

* *Zeitsch. physikal. Chem.*, 1902, **39**, 104.
† Ibid., 1904, **48**, 577.
‡ *Loc. cit.*
§ Ibid., 1903, **43**, 1; 1908, **63**, 1.
|| *Sitzungsber. der Kgl. Bayrischen Akad.*, 1904, **34**, 201.
¶ *Abhandlungen der Bunsen Gesellschaft*, 1909, No. 2.
** *Zeitsch. physikal. Chem.*, 1911, **77**, 513.

(*d*) *The retarded ion hydration hypothesis* of Le Blanc.*
Each of these theories will now be briefly considered.

The Oxide Film Theory.

The mode of action of a film of oxide or other insoluble substance in causing passivity is presumably that it coats the electrode and mechanically hinders metallic ions from entering the solution. Current can only pass when the anode potential is increased to such an extent that anions are discharged.

There can be no doubt that passivity is in some cases due to the formation of an insoluble coating. Thus when lead is anodically polarized in sulphuric acid a coating of lead sulphate forms on the anode and protects the metal against further action. It may be, however, as has been suggested by supporters of other theories of passivity (Foerster) † that such films are in some cases at least a consequence rather than a cause of passivity.

An important investigation which is often cited in favour of the oxide theory is that of E. Müller and Spitzer,‡ who found that on anodic polarization in alkali, iron, cobalt, and nickel became coated with the respective oxides and simultaneously became passive. In order to meet the objection that this might be a secondary phenomenon, they avoided the presence of the metals altogether by examining the behaviour of platinum electrodes coated with the oxides of iron, cobalt, and nickel respectively. Such electrodes on anodic polarization in sodium hydroxide were found to behave in the same way as passive electrodes of the metals themselves, from which the conclusion was drawn that the behaviour of the latter is also due to a coating of oxide.

Haber and Goldschmidt § cite in favour of the oxide theory the observation that iron which has been rendered passive by anodic polarization in alkaline solution without losing its metallic lustre becomes coated with a layer of hydroxide on addition of halogen ions. Le Blanc has made similar observations with nickel anodes, but interprets them in an entirely different way. Haber and Maitland ‖ have shown that in contrast to the behaviour of alkali of moderate concentration very concentrated alkali renders iron active and that it acts by dissolving a superficial film of oxide.

The behaviour of iron electrodes on anodic polarization has yielded results which have been adduced, more particularly by Krassa,¶ in support of the oxide theory. It is well known that iron readily becomes passive by anodic polarization in relatively dilute alkali. Krassa now shows that in boiling concentrated alkali iron can be anodically polarized for some time without losing its activity when the current density is not too large ; on continuing the polarization the anode slowly becomes passive, but great stress is laid upon the fact that the formation of a visible coating precedes passivity. With high current density the anode at once becomes passive.

More recently Grube,** who has made a careful investigation of the electrolytic oxidation of ferrocyanides, has shown that anodes of iron, nickel, cobalt, copper, lead, and silver in neutral solution of potassium ferro- and ferri-cyanide and anodes of iron, lead, silver, and zinc in alkaline solutions of the same salts become strongly passive, and in all cases this is ascribed to the

* *Lehrbuch der Elektrochemie*, 5th edition, p. 285.
† *Loc. cit.*
‡ *Zeitsch. anorg. Chem.*, 1906, **50**, 321.
§ *Zeitsch. Elektrochem.*, 1906, **12**, 49.
‖ Ibid., 1907, **13**, 309
¶ P. Krassa, *Zeitsch. Elektrochem.*, 1909, **15**, 490.
** Ibid., 1912, **18**, 189.

formation of an insoluble coating on the anode. In other cases there is no evidence of an insoluble coating and the passivity is ascribed to an oxygen charge which retards the liberation of cations of the metal.

The weak point in all these investigations is that they were carried out only in neutral or alkaline solution, and therefore cannot afford an explanation of passivity in general, especially in acid solution.

Objections to the Oxide Theory of Passivity.—Very serious objections to the oxide-film theory as an explanation of passivity in general have been adduced by Hittorf, Le Blanc, Fredenhagen, Foerster, and others. These will now be briefly considered.

Hittorf maintains that if the passivity of iron and chromium is to be ascribed to a coating of oxide, such oxides have not so far been discovered, since none of the known oxides possess the necessary properties. The effect of rise of temperature in destroying passivity is very difficult to account for on the oxide theory. Hittorf's so-called "experimentum crucis," whereby chromium, which was capable of decomposing hydriodic acid with the formation of the iodide and liberation of hydrogen, was rendered passive by anodic polarization in a solution of the same acid in the absence of oxygen is also impossible to reconcile with the oxide theory.

Finkelstein * has shown by means of polarization capacity measurements on passive iron that if there is a coating of oxide it must conduct electricity like a metal. He further points out that the assumption of the formation of a definite oxide is difficult to reconcile with the fact that on anodic polarization a metal may take all intermediate potentials from the active to the passive condition. The latter objection is perhaps met to some extent by Haber's discovery that oxide films, in some cases at least, are porous, so that the mechanical hindrance to the escape of metallic ions would presumably increase with the thickness of the coating. A somewhat similar objection was advanced by Fredenhagen,† who applied a gradually increasing or a gradually diminishing e.m.f. to iron, nickel, or chromium electrodes immersed in sulphuric acid and measured the p.d. at the electrodes and the strength of the polarizing current. It was found that when the anode was slowly polarized the potential gradually became nobler, and then there was a rapid change to the passive condition. Conversely, when the electrode was allowed to recover its activity the potential fell gradually at first, and then there was a sudden transformation to the completely active condition. There was, however, no evidence of a definite activity or passivity potential, since the results depended on the concentration of the acid and other factors. These facts are very difficult to reconcile with the assumption that passivity is due to the formation of a definite oxide.

The most serious objection to the oxide-film theory, however, is based on measurements of the reflecting power of metallic surfaces. Müller and Koenigsberger ‡ state that they are able to measure differences of 0·5 per cent. in the reflecting power of two metallic surfaces, and in this way have detected the presence of oxide films of molecular dimensions (0·8 $\mu\mu$ in the case of lead peroxide). Two iron electrodes which had been polarized for some time by generating hydrogen and oxygen respectively in contact with them were found to show no difference whatever in reflecting power, although one was active and the other passive. The objection raised by Haber and Goldschmidt and by Krassa that cathodic polarization with rapid evolution of hydrogen had not reduced the oxide on the surface, and therefore that in both cases the reflecting power of oxidized films was being compared does not seem very convincing.

* *Loc. cit.* † *Loc. cit.* ‡ *Zeitsch. Elektrochem.*, 1907, **13**, 659.

The general impression gained by a review of the evidence is that although the oxide-film theory may apply in certain cases, especially to electrodes anodically polarized in alkaline solution, it can no longer be regarded as a satisfactory explanation of passivity in general.

The Valency Theory of Passivity.

This theory, first brought forward by Finkelstein,* is based on the assumption, due to Krüger,† that the modifications of a metal with different valencies are all present in the solid metal in proportions depending on the temperature and other factors, and that the electrochemical behaviour of metals depends on the relative concentrations of these modifications. W. J. Müller‡ has attempted to find support for this theory from considerations based on the electron theory of conductivity in metals. Both Krüger and Finkelstein recognize, however, that this theory affords no satisfactory explanation of *sudden* changes from the passive to the active condition, nor of the marked effect of the nature of the anion on passivity phenomena. The main point of the valency theory is that the cause of passivity is to be sought in the metals themselves, an assumption which is incompatible with the specific effect of the anions just referred to. The valency theory has met with very little support during the last four or five years, and therefore need not be further considered here.

The Reaction Velocity Theory.

As already mentioned (p. 4) the reaction velocity theory of passivity was first put forward by Le Blanc. One way of stating this theory is that metals in the passive condition send their ions of lowest valency only very slowly into solution. Thus in the case of iron the change represented by the equation $Fe + 2F \longrightarrow Fe^{\cdot\cdot}$ proceeds very slowly when the metal is in the passive condition. This is not to be interpreted in the sense that the actual taking up of electric charges is a slow process (on the contrary, purely ionic reactions are practically instantaneous), but it is assumed that the ionization of the metal is associated with *chemical* changes, and when these changes are very slow, passivity phenomena occur.§ In its general form the reaction velocity theory is little more than a statement of the facts, and attention is mainly directed to the exact nature of the chemical changes associated with the purely electrical changes.

As already mentioned, there are at least four hypotheses as regards the nature of these chemical changes: (*a*) The oxygen charge hypothesis; (*b*) the anion discharge hypothesis; (*c*) the hydrogen activation hypothesis; (*d*) the retarded ion hydration hypothesis.

The Oxygen Charge Hypothesis.—Two or three years after the appearance of Le Blanc's paper on the subject, Fredenhagen || put forward the view that passivity is due to the accumulation of a charge of gaseous oxygen on the metal, the slow reaction being that between metal and oxygen. Sudden changes from the active to the passive condition and vice versa, which sometimes occur, are ascribed to the transition from a non-homogeneous state of polarization into a continuous gas charge covering the electrode uniformly. Even in the latter condition the electrode is not completely inactive, as a slow reaction takes place between it and oxygen.

There is no doubt that the oxygen charge theory represents a considerable

* *Loc. cit.* † *Loc. cit.*
‡ *Zeitsch. Elektrochem.*, 1904, **10**, 832.
§ Compare Foerster, *loc. cit.*, p. 23. || *Loc. cit.*

advance on the oxide-film theory, since (1) it accounts for the effect of rise of temperature in removing activity; (2) it is not inconsistent with the results of optical measurements, since gas charges do not alter the reflecting power of metallic surfaces; (3) it is also, as an irreversible reaction, compatible with Fredenhagen's observation (p. 7) that the curve of gradually increasing activity does not correspond with that of gradually increasing passivity.

There are, however, formidable objections to the oxygen charge theory, of which the following may be mentioned:

(1) It does not account for Hittorf's "experimentum crucis" on the passivity of chromium in hydriodic acid (see above).

(2) Certain metals which can be rendered passive combine readily with oxygen under other circumstances, and no explanation is afforded of their assumed inactivity towards this gas when in the passive state.

(3) It does not account for the fact recently established by Grave,* that iron becomes passive on heating in nitrogen.

(4) It affords no explanation of the passivating effect of alkalis on iron.

For these reasons the oxygen charge theory cannot be regarded as affording a satisfactory explanation of passivity phenomena.

The hypothesis of primary anodic discharge, first put forward by Sackur,† promises to play a considerable part in the future development of electrochemistry. It has been generally assumed that when a metal dissolves at the anode, the primary process consists in a passage of the metal into solution in the form of ions. Sackur put forward his hypothesis of primary anion discharge without much experimental proof, for some time it met with little acceptance. Recently, however, support has been lent to this hypothesis by the observation of Haber and Zawadzki‡ that when solid compressed silver salts are electrolysed between electrodes of silver considerable polarization occurs, and this polarization is greatly increased by lowering the temperature. The probable explanation is that the transport of the current from solid electrolyte to anode is effected by the passage of negative electrons from anions to metal; the discharged anions then attack the silver anode, the latter change being greatly retarded by cooling. It is not improbable that the mechanism of current transport is the same in aqueous solution, but in this case the discharged ion in presence of the solvent reacts rapidly with the electrode, so that little or no polarization occurs.

It is evident that the above considerations afford an explanation of passivity phenomena on the basis of the reaction velocity theory. Sackur's explanation is rather complicated. He assumes that every electrode contains a certain amount of dissolved hydrogen formed by interaction with $H^{\cdot}$ ions in the electrolyte; the hydrogen concentration corresponds to the equilibrium represented by the equation (for a bivalent metal)—

$$Me + 2H^{\cdot} \rightleftharpoons H_2 + Me^{\cdot\cdot}.$$

The discharged anion (oxygen, halogen, etc.) reacts with and removes the hydrogen. To re-establish equilibrium the above reaction then proceeds in the direction of the upper arrow, so that the anodic dissolution of metals is a chemical process. Passivity is brought about by a slow rate of reaction between the hydrogen and the discharged anion, so that the latter (oxygen, etc.) accumulates on the electrode. There is considerable resemblance as regards the final stage between this hypothesis and the gas charge hypothesis. Although the above hypothesis is very suggestive, it is in one

* *Loc. cit.* † O. Sackur, *Zeitsch. Elektrochem.*, 1908, **14**, 612.
‡ *Zeitsch. physikal. Chem.*, 1911, **18**, 228.

respect self-contradictory, as has been pointed out by Auerbach.* It starts with the assumption that the metals do not primarily ionize, whereas the assumed interaction of the metal with hydrogen is just such an ionization.

The hydrogen activation hypothesis, based on the assumption that the *pure* metal is passive and only becomes active under the influence of a catalyst, was put forward by Foerster † on the basis of a very detailed investigation of the electromotive behaviour of iron. If the reaction velocity theory, that passivity is due to the slow rate of ionization of the metal, is correct, then since the reaction $Fe + 2F \rightleftarrows Fe^{\cdot\cdot}$ is reversible, the converse process, the electrolytic precipitation of iron, will probably also be a retarded reaction, a deduction which is fully confirmed by experiment.

Foerster points out that the hydrogen activation theory is in agreement with the effect of cathodic polarization and of acids in promoting activity, also with the behaviour of iron in air, under the influence of oxidizing agents, in the presence of alkali, etc. He does not deny that oxide films may play a part in passivity phenomena in certain cases, but considers that the production of such films is a consequence rather than a cause of passivity. In the case of anodic polarization of iron in alkali, for instance, the underlying cause of passivity is the absence or removal of hydrogen, and the deposition of an oxide follows on account of the inactive condition of the metal. The chief advantage of this theory over the oxide theory is that it is valid both for polarization in acid and alkaline solution. It is pointed out that other substances than hydrogen may facilitate the reaction $Fe + 2F \longrightarrow 2Fe$; for instance, the presence in solution of substances capable of taking up negative or giving up positive charges, such as the halogens or metallic ions of higher valency, *e.g.*, $Fe^{\cdot\cdot\cdot}$. It is well known that the dissolution of passive metals is greatly facilitated by the presence of such substances.

Strong support has been given to Foerster's hypothesis by Grave, ‡ who, however, contends that the catalyst is not hydrogen, or an alloy of hydrogen with the metal, as Foerster assumes, but hydrogen ions. In favour of this view the following facts are adduced. Iron and nickel become active when heated in hydrogen, but become passive when strongly heated in air, nitrogen, or a vacuum. Molecular hydrogen, after being in contact with iron and nickel, does not alter the potential, but ionized hydrogen renders the metals active, and ionized nitrogen renders them passive. Hydrogen ions are given off when a metal changes from the active to the passive state. When iron is saturated with $H^{\cdot}$ ions, the charge given off on heating is greatly increased. When iron is rendered active at one point by bringing it in contact with hydrogen ions, other parts of the metal are rendered active by diffusion. This explanation of passivity has also been shown to afford an explanation of the well-known periodic phenomena at electrodes of chromium and other metals which can be rendered passive. §

Quite recently, Flade and Koch ‖ have attempted to decide between the oxygen and hydrogen theories of passivity as follows : If an active electrode is heated and means are taken to remove any hydrogen given off, the metal must become passive if the hydrogen theory is correct, and active if the oxygen theory is valid. Further, if passive iron is heated in a vessel containing a reducing gas which is neither hydrogen nor a compound containing hydrogen, the metal must remain passive if the hydrogen hypothesis applies, and must become active if the oxygen hypothesis is valid. It was found that

* *Zeitsch. Elektrochem.* † *Loc. cit.*
‡ E. Grave, *Zeitschr. physikal. Chem.*, 1911, **77**, 513.
§ A. Adler, ibid., 1912, **80**, 385.
‖ *Zeitschr. Elektrochem.*, 1912, **18**, 335.

an active iron electrode remained active on heating in a vacuum, which speaks in favour of the oxygen theory. On the other hand, iron which had become passive by standing in air remained passive when heated in carbon monoxide, which appears to be contrary to the oxygen theory. It was found, however, that heating in carbon monoxide also renders active iron passive, and the author maintains that the result of the second experiment is also compatible with the oxide theory. With reference to the first experiment, the possibility of an objection to the effect that the metal after heating in a vacuum may still contain traces of hydrogen is foreseen, but is not regarded as valid.

Le Blanc's Views.—As Le Blanc was the first to put forward the reaction velocity theory of passivity, his views on the later developments of the subject are naturally of interest. I cite them according to the latest edition of his *Lehrbuch der Elektrochemie.** Foerster's suggestion that pure iron is the passive form and that it only becomes active in the presence of a catalyst is apparently not accepted. It is assumed that active iron sends out ions into the electrolyte, and that in the case of metals which tend to become passive these ions only combine very slowly with water, according to the equation—

$$\text{Ion} + \text{water} \rightleftarrows \text{ion hydrate}.$$

On this account the concentration of free ions at the electrode becomes so great, and therefore the potential difference between electrode and solution becomes so considerable, that the discharge of anions or of oxygen begins. This hypothesis of passivity is based on the observation that even when the ion concentration at the electrode is sufficiently large, polarization occurs both at anode and cathode in many cases where it was not previously suspected.† In order to explain these facts a difference between free and hydrated ions is postulated, and it is assumed that the hydration and dehydration of ions is under certain circumstances a relatively slow process. It should be mentioned that this assumption is due in the first instance to Foerster and Luther,‡ and was applied by Foerster to account for the retardation observed in the discharge of $Fe^{\cdot\cdot}$ ions at an iron cathode. It may further be added that although the view that ions are more or less hydrated has met with wide acceptance, there does not appear to be any independent evidence of the slow hydration which forms the basis of Le Blanc's theory of passivity.

Conclusion.

The more important phenomena of passivity have now been briefly discussed, and the chief theories which have been put forward to explain these phenomena have been described. The main object of this paper is to afford a résumé of the present position of the subject, and it would be out of place in opening the discussion to attempt any detailed comparison of the relative merits of the different theories. This can be more profitably attempted when the various contributions to the discussion are available.

In all probability it will eventually be found that no one theory will serve to account for all the phenomena of passivity. Thus both Le Blanc and Foerster, although in the main favouring other explanations, recognize that the formation of insoluble films on the electrodes plays a part in some cases of passivity. The hydrogen activation theory, which is perhaps most in favour at the moment, is undoubtedly valid to some extent, as the effect of nascent hydrogen § in restoring the activity of passive metals is beyond

* Fifth edition, p. 283.

† Le Blanc, *Abhandlungen der Bunsen Gesellschaft*, No. 3, 1910.

‡ Foerster, *loc. cit.*, p. 55.

§ According to Hittorf and Grave *molecular* hydrogen does not restore the activity of passive metals.

dispute. Whether iron entirely free from hydrogen is necessarily passive, as Foerster and Schmidt assume, would, however, appear to be still open to discussion. In particular, the activating influence of the free halogens (*e.g.*, iodine in potassium iodide) is difficult to reconcile with this view, as it would appear that the metal in the absence of hydrogen is capable under these circumstances of sending charged ions freely into solution, which is contrary to the theory. On the other hand, it should not be difficult to devise a plausible explanation of the *sudden* changes from the active to the passive state and vice versa on the basis of the hydrogen activation theory, whereas these changes are difficult to reconcile with any of the other theories. It is not easy to understand, for instance, how such sudden changes could occur on the basis of the ion hydration hypothesis favoured by Le Blanc.

ANODIC AND KATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

(Translated from the German.)

Professor G. Grube (Dresden) read a Paper on "Anodic and Kathodic Retardation Phenomena and their bearing upon the Theory of Passivity."

There used to be a general tendency to assume that both the formation of metallic ions in the anodic dissolution of a metal and the transition from the ionic into the metallic state in kathodic deposition were processes which took place at a practically infinite velocity. On that view a metallic anode, immersed in a solution of one of its salts, should with anodic polarisation pass into solution as soon as the equilibrium potential was slightly exceeded which the respective electrode possessed in that solution. Some rise in the potential above the equilibrium value, and thus some polarisation, was to be expected only in so far as it would be demanded, according to the formula of Nernst, by an increase in the concentration in the immediate neighbourhood of the anode. In cases where a higher polarisation was noticed, such that potentials were attained which permitted of an evolution of oxygen simultaneous with the dissolution of the metal, or merely of an evolution of oxygen unaccompanied by a formation of metallic ions, the cause of this "passivity" was frequently ascribed, with Faraday, to the formation of a film of oxide on the electrode. It was the great merit of M. Le Blanc to have pointed out† that, with certain metals, the passivity finds its explanation in the circumstance that these metals emit their ions of lowest valency into the solution at a greatly restricted velocity.

Since now it is a fact that, in the case of one and the same metal which can be rendered passive, the formation of kations takes place at a much more rapid rate when it is in the active state than when in the passive state, we have to ask ourselves how these great variations in the velocity of reaction can arise. There were two possible explanations: either we supposed the rate of formation of ions in the active state to be characteristic of the metal—in that case the retardation of the velocity of reaction in the passive state had to be attributed to the effect of a negative retarding catalyst; or we assumed the passive state of metals (which can be passivated) to be the normal state—in that case the marked acceleration in the formation of the ions in the active state could only be due to the effect of some accelerating catalyst. Both these possibilities have been taken into consideration. W. Muthmann and

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden.

† *Zschr. Elektrochem.*, 6, p. 472 (1900); *Lehrbuch der Elektrochemie*, 3rd edition p. 237 (1903).

Fraunberger,* as well as Fredenhagen † suggested that a solid solution of oxygen is formed on the surface of the metal (which can be rendered passive) when it is anodically polarised or treated with oxidising agents, and that this fact causes the retardation in the emission of ions. F. Foerster,‡ on the other hand, advocated that the passive state was normal for certain metals, and that the accelerated formation of kations from these metals in the active state was due to the hydrogen adsorbed by the metallic surface. Foerster was led to this view by the observation, which he and others had frequently made, that whenever iron became active, hydrogen was liberated at it. It was further known that iron, from which hydrogen had once been evolved, could take up small quantities of hydrogen and would thereby change its properties in the sense that it became highly reactive chemically. The potential of an iron electrode, kathodically polarised with hydrogen, against normal ferrous sulphate also shows less noble values than would correspond to the equilibrium of pure iron with regard to that solution.§ The hypothesis hence appears plausible that it is hydrogen which catalytically accelerates the emission of ions from the iron. It will be understood that, like Le Blanc, Foerster finds the cause of the passive state in a diminution of the rate of kation formation. It is a consequence of the strongly retarded formation of ions from metals which can be passivated, that these metals, when anodically polarised, easily assume potentials which correspond to a weak charge of the electrode with oxygen. This oxygen, which in the first instance is a consequence of the passivity, will in its turn be able to impede still more the in itself retarded process of ion-formation at the anode, and will thus lead to a further rise of the anode potential ; this potential will finally attain values such that oxygen liberation sets in at the anode in addition to the formation of metallic ions, and that this oxygen liberation may claim the main share of the polarising current. A complete cessation of the formation of metallic ions owing to the impeding action of the oxygen charge is, however, rare. There will thus be a possibility that the kations emitted from the anode at small rate will combine with the oxygen taken up by the anode surface to oxidic precipitates which, like the oxygen charge, must be regarded as a secondary consequence of the passive properties of the anode metal, not as their cause.

That the fundamental view of the theory of passivity of Le Blanc as just outlined is correct, that is to say, that both anodic dissolution of a metal and kathodic deposition of a metal may be retarded phenomena, has within recent years been established by many experimental researches.|| It would lead us too far to discuss the results of all these researches. I will content myself with dealing with the second part of Foerster's passivity theory, according to which the small velocity of reaction marking the anodic dissolution and the kathodic deposition of passive metals does not alone suffice to focus the whole domain of activation and passivation, and that we are hence forced to assume a co-operation of positive and negative catalysts on the electrode. The following important question thus suggests itself as concern-

* *Sitzber. Bayer. Akad. Wissensch.*, 34, p. 201 (1907).

† *Zschr. Physik. Chem.*, 43, p. 1 (1903) ; *Zschr. Elektrochem.*, 11, p. 857 (1905) ; *Zschr. Physik. Chem.*, 63, p. 1 (1908).

‡ *Abhandlungen Bunsen-Ges.*, No. 2 (1909).

§ *Abhandlungen Bunsen-Ges.*, No. 2, p. 9 (1909).

|| Cf., *e.g.*, M. Le Blanc and M. G. Levi, *Annal. d. Physik.* (Boltzmann Festschrift), 1904, p. 183 ; F. Foerster, *Abhandl. Bunsen-Ges.*, No. 2 (1909) ; M. Le Blanc, ibid., No. 3 (1909) ; A. Schweitzer, *Zschr. Electrochem.*, 15, p. 602 (1909) ; R. Schildbach, ibid., 16, p. 967 (1910) ; H. G. Byers, *Journ. Amer. Chem. Soc.*, 30, p. 1718 (1908) ; E. P. Schoch, *Trans. Amer. Electrochem. Soc.*, 14, p. 99 (1908) ; E. P. Schoch and C. P. Randolph, *Journ. Phys. Chemistry*, 14, p. 719 (1910), etc.

ing the problem of passivity : In how far is the velocity of reaction, and hence the variation of the potential in anodic and kathodic processes, influenced catalytically by the occurrence of small quantities of foreign substances on the surface of the electrode ?

I should like now to place before you some experimental researches which F. Foerster and his pupils have undertaken within the past few years in order to answer that question. In the first instance I propose to dwell upon the retardation observed in the emission and deposition of metallic kations ; I shall afterwards touch upon the retardation phenomena which occur in the discharge of anions.

Le Blanc * on the one hand, and F. Foerster † and his pupils on the other, had found that the kathodic deposition of the metals of the iron group takes place at a diminished rate. This process now, as F. Foerster has demon-

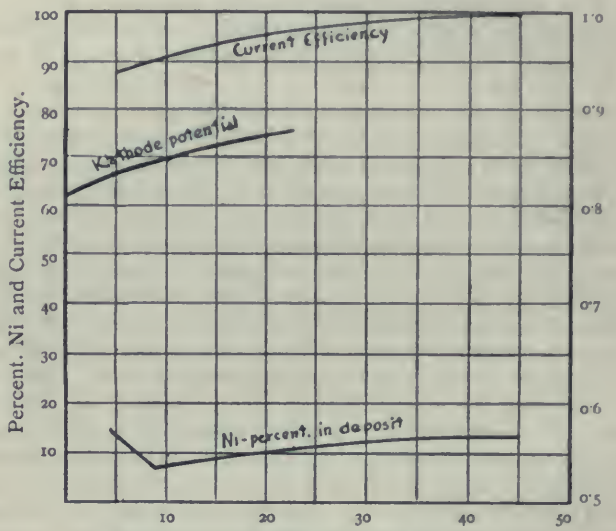


FIG. 1.

strated in conjunction with W. Treadwell, jun., and W. von Escher, may undergo a further retardation when there are also present small quantities of zinc on the surface of the kathodically deposited iron-metal.

The experiments of W. Treadwell ‡ were undertaken in order to inquire into the fact which had almost at the same time been established by E. P. Schoch and A. Hirsch,§ that, from a solution which contains in addition to an excess of nickel sulphate some zinc sulphate, kathode deposits may be obtained at ordinary temperature which will be decidedly richer in zinc than in nickel. Treadwell's results were the following : At ordinary temperature solutions, in which the nickel sulphate is in excess, yield a deposit in which zinc predominates ; this is so at all the current densities at which any metallic deposits can be secured. The kathode potential assumes during the

* *Abhandl. Bunsen-Ges.*, No. 3 (1909).

† Ibid., No. 2 (1909) ; A. Schweitzer, *Zschr. Elektrochem.*, 15, p. 602 (1909) ; R. Schildbach, ibid., 16, p. 967 (1910).

‡ *Dissertation*, Zürich (1909) ; cp. also F. Foerster, *Zschr. Elektrochem.*, 17, p. 883 (1911).

§ *Journ. Amer. Chem. Soc.*, 29, p. 314 (1907).

electrolysis values which come up very close to those of a pure solution of zinc sulphate at corresponding current densities. Fig. 1 exemplifies the results of a series of experiments conducted at 18° with a solution which was 0·5 N as regards the zinc sulphate and the nickel sulphate, and 0·01 N as regards the sulphuric acid. The percentage of nickel in the kathode deposit, the kathodic current efficiency and the variation of the kathode potential with the current density are plotted in the diagram. It will be seen that the nickel percentage is very low even at small current density; the percentage decreases to a minimum, and rises very slowly afterwards. The current efficiency also rises with increasing current density, from 90 per cent. to 95 per cent. at high density; thus little current is spent in the generation of hydrogen.

The same solution yields essentially different results at 80°, however, as the experiments plotted in Fig. 2 will show. In this case the deposits, as long as the current density is kept low, are rich in nickel and resemble

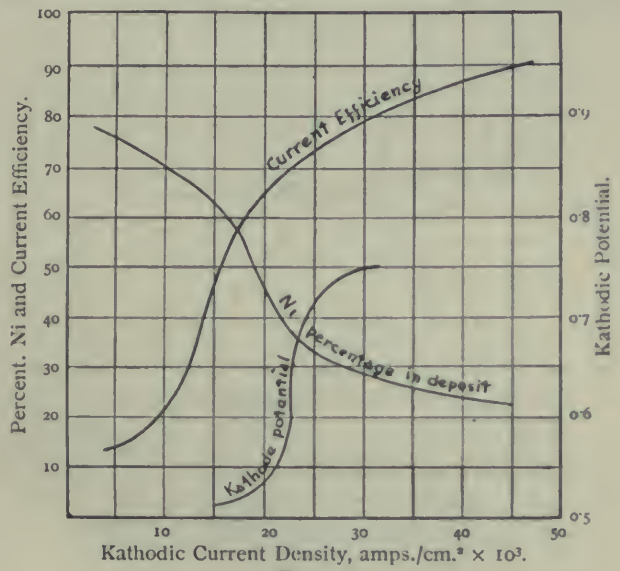


FIG. 2.

nickel in appearance. When the current density is raised, the nickel percentage of the deposit falls off, very rapidly at first, more slowly afterwards. The deposition of the alloy rich in Ni takes place at potentials at which, in the absence of zinc, the solution would have thrown down nickel only. When, however, with increased current density, the Ni percentage of the deposit is lowered and the alloys become richer in Zn, the kathode potential likewise rises suddenly to values approaching that required for the deposition of zinc. The current efficiency curve takes a similar trend. At low current density the efficiency remains below 20 per cent.; the current is mainly spent in liberating hydrogen, therefore. When the kathode potential jumps up to that of base metals, with increasing current density, the current efficiency also rises rapidly.

The retardation phenomena occurring in the electrolysis of solutions containing zinc sulphate and ferrous sulphate are somewhat more pronounced still, as W. von Escher has shown.* If we start from solutions

* *Dissertation*, Dresden, 1912.

which are equally concentrated as to zinc and iron, the alloys deposited, not only at ordinary temperature, but also at 90°, at very small current density, consist predominantly of zinc. To obtain alloys rich in iron, at low current densities and high temperatures, is only possible when there is a decided excess of ferrous sulphate over the zinc sulphate. Fig. 3 exemplifies an experiment conducted at 90°; the solution was 0·01 N acid, and the ratio of Fe to Zn was 9 : 1·5. Although the temperature was high, it will be recognized the transition from deposits rich in Fe to deposits rich in Zn took place already at very low current density. The deposit potentials were, for the alloys rich in iron, those which (as resulted from special experiments) were required for the deposition of pure iron from solutions of ferrous sulphate of equal concentration. When, however, at higher current densities the transition-point to the deposits consisting essentially of zinc had been passed, the kathode potential assumed the value corresponding to pure zinc.

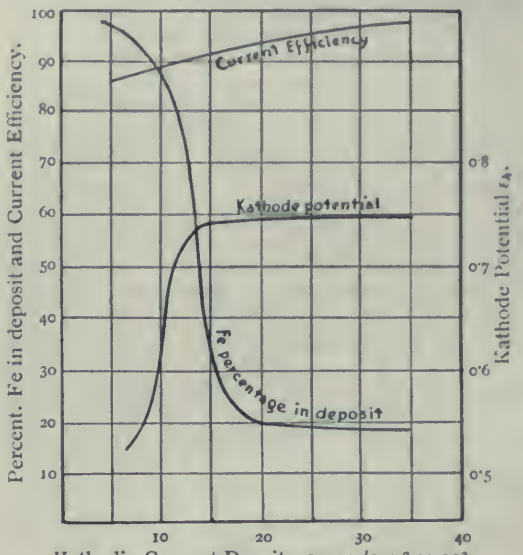


FIG. 3.

The current efficiency was somewhat below 90 per cent. at low current density, and a little above that value at high current density. Further experiments made at the same temperature (90°) showed that when the ratio Fe : Zn was varied in favour of iron, the transition-point from predominantly iron deposits to zinc deposits was shifted into the region of higher current density. In one series of measurements, in which the concentration ratio was Fe : Zn = 9 : 0·63, but which otherwise agreed with the former, the transition occurred only at the density 0·035 or 0·040 amp./cm.² On the other hand, any lowering of the temperature or an increase in the zinc concentration shifted the transition into the region of low current density, or suppressed it altogether, the deposits remaining rich in zinc at all the current densities. The concentration of the hydrogen ions also has an influence upon the transition. In a solution of 0·01 N acidity and a concentration ratio Fe : Zn = 9 : 1, the transition was observed at the current density 0·022 amp./cm.² at 90°; in a neutral solution of the same concentration, however, the deposits were poor in zinc up to current densities of 0·040 amp./cm.² In this latter case the

transition did not take place, therefore. It could be produced, however, also in neutral solutions by raising the zinc concentration. With the concentration ratio Fe : Zn = 9 : 1·5, *e.g.*, the transition was observed at 90°, in neutral solution, between the current densities 0·020 and 0·025 amp./cm.^{2} The zinc proportion of the kathode deposit, at which transition occurred, was 11 per cent. however, whilst 5 per cent. sufficed with 0·01 N acidity to raise the potential to the value necessary for the zinc preponderance. The transition was thus more easily realized in the latter case, which is further indicated by the circumstance that a current density of 0·010 amp./cm^2. was sufficient.

When we summarise the results of Treadwell and Escher we find that in solutions of nickel sulphate and ferrous sulphate, which further contain zinc sulphate, the electrolysis at ordinary temperature yields deposits consisting predominantly of zinc. When the electrolysis is performed at higher temperatures, it is possible under suitable conditions of low current density to obtain also deposits poor in zinc. These latter deposits are realized at low current efficiency and at potentials which would likewise be recorded in depositing pure iron or pure nickel from the same solution not containing any zinc; the formation of the former deposits takes place at considerably higher current efficiency, at the potential necessary for the deposition of zinc.

The explanation of these phenomena may first be given with regard to higher temperatures: at small current density the metals nickel and iron are deposited on the kathode at the potential required for their deposition from pure solutions; at the same time that amount of zinc must be deposited which corresponds to the concentration of the zinc ions at the kathode and to the kathode potential. This amount is in itself very small; since, however, both iron and nickel can absorb a good deal of zinc with formation of alloys, considerable amounts of zinc will have to be deposited in order to get into equilibrium as regards kathode potential and concentration of zinc ions. In this way an alloy poor in zinc is formed at the potential of the more noble metal, and the further deposition of iron or nickel on this alloy is effectually retarded. Consequently the hydrogen liberation will predominate. When now the current density is raised, the concentration of the hydrogen ions in the weakly acid solution will no longer satisfy the current, and polarisation is set up; thus the zinc potential is attained. The hydrogen liberation then diminishes, and zinc is chiefly deposited in addition to some more iron and nickel.

At ordinary temperature the separation of nickel and iron even from their pure solutions is much more difficult than at higher temperature.* The retardation of their deposition from the solutions mixed with zinc sulphate will hence be so great from the very first, that only alloys rich in zinc will result at the zinc potential. Thus the experiments described offer the interesting phenomenon that the kathodic passivity of iron and nickel is so much strengthened by the original co-precipitation of zinc, that the deposition of these metals almost ceases and that, at a potential which is by 0·2 volt less noble than that required for the deposition of pure iron and nickel, a kathode deposit will be formed which will essentially consist of zinc. The intensity of this polarisation apparently depends also on the concentration of the hydrogen ions in the electrolyte, because Escher has proved that the rapid rise in the potential takes place with greater difficulty in neutral than in weakly acid solutions. The acidity of the electrolyte hence acts in the sense of an increase in the zinc concentration, *i.e.*, it intensifies the polarisation.

* Cp. A. Schweitzer, *loc. cit.*, and F. Foerster, *loc. cit.*

This fact induced us to compare the polarising effect of zinc with the phenomena which accompany the deposition of iron, cobalt, and nickel from the acid solutions of their simple salts. According to F. Foerster's experiments on iron,* those of R. Schildbach † on cobalt, and of M. Schade ‡ on nickel, the deposition potential is in these reactions strongly influenced by the concentration of the hydrogen ions in the electrolyte, the effect being such that increased acidity leads to a higher polarisation, other conditions being equal.

The question now arises, how can we account for the polarisation phenomena accompanying the deposition of the iron metals which, as we have seen, are intensified by the presence of zinc sulphate or of hydrogen ions. Le Blanc has expressed the opinion that the metals form ionic hydrates, whose existence is also assumed for other reasons, and that the supplementary supply of metallic ions (for the deposition of the metal) from these hydrates takes place at a restricted velocity only. On this view the moderate velocity of the reaction—

$$Me_n(H_2O)^{++} \rightleftarrows Me_n^{++} + H_2O$$

in the direction left to right would be the cause of the high polarisation in the deposition of the metals, and the increase in the polarisation, observed in the presence of zinc sulphate or acid, would occur because these additions much retard the decomposition of the ionic hydrates. Such an inhibitory action is possible; it appears little plausible, however. It seems preferable to look for the cause of the retardation of the kathodic reaction in some change of the kathode surface. We may suppose that alloys containing zinc or hydrogen are deposited on the kathode, and they possess a higher electrolytic solution pressure than the pure nickel or iron. The formation of the—for the present purely hypothetical—intermediate products would then be the cause of the marked retardation in the deposition of the metals.

The experiments which have been mentioned clearly demonstrate, at any rate, that a retarded kathodic process may undergo a further pronounced retardation when the kathode takes up foreign matter. If that be granted, the assumption which is made in explanation of the anodic passivity, namely, that slowly-proceeding anodic reactions are further and essentially retarded by the formation of oxygen alloys in the surface of the anode, gains a higher degree of probability. In addition to this passivity which is due to an oxygen charge, there will also be a possibility of passivity during the anodic dissolution of metals in cases where the kations emitted by the anode will be able to form a scarcely soluble compound with the anions of the electrolyte. We shall only then be justified in ascribing the passivity to surface films if such films may be expected to form in accordance with the chemical behaviour of the electrolyte near the anode. When the causes of the anodic passivity are discussed, the question will therefore not be quite general, whether any retardation in the emission of the ions may arise from the formation of an oxygen alloy on the surface of the anode, or whether the retardation be caused by the mechanical closure (covering up) of the surface of the electrode by the formation of an oxide skin or of some other scarcely soluble precipitate. According to the conditions of the experiment, the one or the other moment will cause passivity.

I now wish to refer to some experiments of mine § which show that, at one

* *Loc. cit.* † *Loc. cit.* ‡ *Dissertation*, Dresden, 1912.
§ G. Grube, *Zschr. Elecktrochem.*, 18, p. 189 (1912).

and the same electrode metal in the same electrolyte, there may, according to the experimental conditions, be a passivity of the surface films, as well as a passivity due to an oxygen charge, and that, under suitable conditions, the two phenomena may continuously pass into one another. The experiments were undertaken, in the first instance, for the purpose of inquiring into the suitability of various metals as electrodes for the electrolytic preparation of ferripotassium cyanide. I determined current density-potential curves with anodes of the several metals in neutral and in alkaline solutions containing both ferro- and ferripotassium cyanide. The sheet metals were dipped into the electrolyte ; the potential was measured first without current ; the electrode was then anodically polarised while the electrolyte was well stirred, and the current density was raised, and the potential was determined in the usual way.

We are on this occasion interested only in the results obtained with the metals platinum, gold, iron, nickel, cobalt, and copper. The polarisation phenomena varied to an extraordinary degree with the experimental conditions. When the electrolyte was a neutral solution with a total content (of

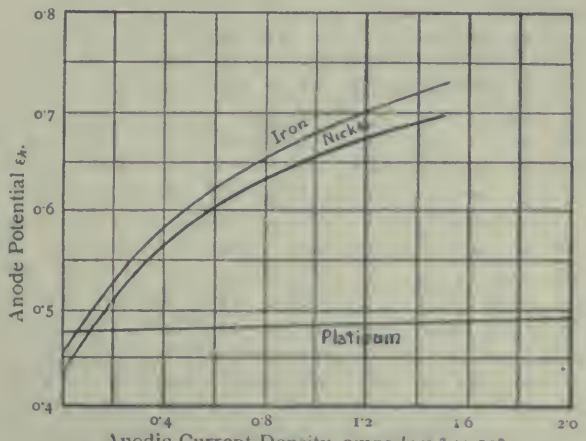


FIG. 4.

ferropotassium cyanide + ferripotassium cyanide) of 0·5 mol, whilst the ratio $K_4FeCy_6 : K_3FeCy_6$ in the solution was 25 : 75 or 75 : 25, the potential found, when the current was not flowing, with platinum and gold electrodes was the oxidation potential of the respective solution, whilst much less noble potentials were observed with iron, cobalt, nickel, and copper ; these latter potentials gradually became more noble, however. The latter electrodes at the same time became covered with films of their sparely soluble ferrocyanogen compounds. Thus gold and platinum were completely passive in neutral solutions, whilst iron, nickel, cobalt, and copper behaved at first like soluble electrodes which gradually became covered with surface films and assumed the nobler, passive potential. When the electrodes were now anodically polarised, gold and platinum too showed the small polarisation (due to changes in concentration), whilst an extraordinarily intense polarisation was noticed on the other electrodes, which were covered with surface films. The current density-potential curves observed with iron, nickel, and platinum in neutral solutions are reproduced in Fig. 4. We see how very strong the polarisa-

tions are in the first two cases (anodes with surface films) compared with the concentration polarisation of the platinum anode.

The aspect changed very materially when the same solution of ferro- and ferricyanide was rendered 0·1 N alkaline by the addition of KOH. In this solution not only gold and platinum but also iron, cobalt, nickel, and copper marked, when not under current, the oxidation potential of the electrolyte; the appearance of a surface film was no longer noticeable in any case; all the metals remained perfectly bright. When the electrodes were anodically polarised in this instance, the same small concentration polarisation was shown by all the metals except iron. Iron yet indicated in the alkaline solution a pronounced polarisation which could considerably be diminished, it is true, by increasing the alkalinity of the electrolyte and by raising the temperature, but which could never be reduced to the low values measured at the other metals. In these experiments, however, the eye could not discern the formation of any surface films on the iron. But the film was visible when the experiment was made in a 0·01 N alkaline solution. In this solution the iron electrode marked, a short while after immersion, a potential which was by 8 millivolts less noble than the oxidation potential of the solution. Within half an hour, however, the iron potential had risen to this value, while the electrode became covered with a faintly discernible layer of Prussian blue, which was gradually decomposed by the alkali of the electrolyte and converted into an oxide film. This oxide film could only be seen in some spots; the rest of the surface appeared quite bright. Under anodic current this electrode gave a still higher polarisation than had been noticed in the 0·1 N alkaline solution. The existence of an invisible oxide film had, however, to be presumed also in more strongly alkaline solutions, since the polarisation was gradually seen to increase in them when the current intensity was kept constant and the electrolyte remained unchanged. Thus in an 0·1 N alkaline solution, *e.g.*, the polarisation rose, at 0·002 amp./cm.², in 265 minutes from 90 up to 134 millivolts. These observations indicate that in all probability the passivity of the iron electrode in alkaline ferro-ferricyanide solutions was also due to the formation of an oxide film.

On the contrary, the passivity of electrodes which showed merely concentration-polarisation in alkaline solutions could not be attributed to an oxide film of similar kind as with the iron electrode. This was concluded, in the first instance, from the non-observance of any increasing polarisation, and further from the following experiments:

When by suitable previous treatment a very thin translucid oxide film had been produced on electrodes of nickel or cobalt, these electrodes showed, in alkaline ferro-ferricyanide solutions, at once the same polarisation phenomena of the same order of magnitude as iron electrodes. If, therefore, the passivity had on nickel, cobalt, and the other metals which were not polarisable in alkaline electrolytes, been caused by the same kind of oxide layers, this passivity should have called forth an intensified polarisation. As this was not the case, we should have been forced—provided we declined to abandon the surface layer as cause of the polarisation—to assume that these surface films responsible for the passivity were good conductors, capable indeed of impeding the emission of kations, but not of opposing any resistance to the passage of the current. The existence of such well-conducting films is, however, extremely improbable, since the oxide skins formed by purely chemical means introduced a considerable polarisation.

If, in spite of that, it should be suggested that the passivity films were of the same kind as those chemically prepared, but of so insignificant a thickness that they could not give rise to any pronounced polarisation, we should have

to imagine that the oxidations of ferrocyanide were taking place under the co-operation of some peroxide in the oxide layer. We could not conceive then, however, why such peroxides, whose existence we should have to assume for the different metals gold, platinum, nickel, cobalt, and copper in alkaline solutions, should all be able to effect the oxidation of the ferrocyanide at the same potential and with the same velocity. On account of this equality of the potential, at which the oxidation of ferro-ferricyanide solutions is taking place with different metals, we shall have to suppose that there is no oxide film on these metals (which cannot anodically be polarised), but that these metallic surfaces are in perfect contact with the electrolyte. Since therefore the presumption of oxide films does not afford any unstrained explanation of the cause of the passivity of platinum, gold, nickel, cobalt, and copper, it appears apposite to trace their passivity back to a retardation in the emission of kations consequent upon the charge of the anode with oxygen.

Such oxygen charges must doubtlessly exist, to judge from the position of the potentials of the anodes in the anodic oxidation of ferro-ferripotassium cyanide solutions. We must further suppose these charges to be stronger in alkaline than in neutral solutions, since they must be in equilibrium with the concentration of the hydroxyl ions in the electrolyte. The last-mentioned fact was proved by Fredenhagen* by comparing the potentials of alkaline ferro-ferripotassium cyanide solutions with the potentials of oxygen electrodes in alkali solutions of equal concentrations. It resulted that the former potentials were more noble than the latter (oxygen) potentials, and that this potential difference increased with increasing alkali concentration of the electrolyte. That shows that the oxygen pressure acting upon an electrode immersed in an alkaline ferro-ferricyanide solution is likewise increased by the higher alkaline concentration of the electrolyte. The pressure is materially smaller in a neutral ferro-ferricyanide solution than in an alkaline solution. Thus it comes about that nickel, cobalt, and copper are still able to emit kations into the electrolyte in neutral ferro-ferricyanide solutions, but that the rate of ion formation has practically dwindled to zero in alkaline solutions, owing to the increased oxygen charge. In the case of iron the rate at which ions can be formed is likewise much diminished in alkaline solutions. It is yet sufficient though to cause the formation of oxide films. The passivity phenomena of the experiments described mainly depend upon the special position of the ferro-ferripotassium cyanide potential, and it is entirely within the range of possibility that, at more noble potentials, the metals examined would show a very different behaviour.

The question in which way the oxygen charge of the anode impedes the emission of kations from the anode cannot yet be answered. If we assume with O. Sackur,† as well as with F. Haber and J. Zawadsky,‡ that the primary process of the anodic polarisation of a metallic electrode signifies in every case, and therefore also in the case of a soluble anode, the discharge of the anions, then the passivity phenomena which we have been discussing would have to be considered from the same point of view as the retardation of the discharge of halogen ions from platinum electrodes. It has long been recognised § that, especially with smooth platinum, the discharge of the halogens from solutions of the halides takes place at potentials which are

* *Zschr. anorgan. Chem.*, 29, p. 396.
† *Zschr. Elektrochem.*, 10, p. 841 (1904).
‡ *Zschr. Physik. Chem.*, 78, p. 228 (1911).
§ Cp. E. Müller, *Zschr. Elektrochem.*, 6, p. 573 (1900); 7, p. 750 (1901); 8, p. 424, (1902); Luther and Brislee, *Zschr. Physik. Chem.*, 45, p. 216 (1903); Böricke, *Zschr. Elektrochem.*, 11, p. 71 (1905); Pfleiderer, *Zschr. Physik. Chem.*, 68, p. 49 (1909).

materially more noble than we should expect from the position of the equilibrium potentials of the halogens in the respective solutions.

A systematic investigation by F. Foerster and J. Yamasaki* of the phenomena which accompany the discharge of bromine from neutral and alkaline potassium bromide solutions, had established that the anodic discharge of bromine ions from platinised platinum anodes was only then reversible, when the anode in question was free from any oxygen charge. When, however, the anode was charged with oxygen, be that by anodic polarisation or by a liberation of oxygen during the electrolysis of the bromide, the discharge of the bromine took place at potentials considerably more noble than those one might have expected for the reversible reaction from the observed bromine potentials. Thus an oxygen content of the platinised electrode retards the discharge of the bromine ions.

Quite recently F. Foerster and F. Herrschel† have also studied the retardation of the iodine discharge from iodide solutions. The electrolysis of neutral and of alkaline solutions of potassium iodide, it resulted, did not in

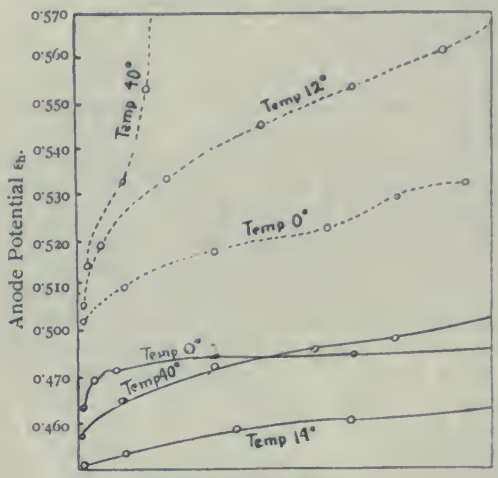


FIG. 5.

general prove strictly reversible. The anode showed temporarily increasing polarisations, much more intense than concentration effects, and this temporary rise of the potential was much greater with smooth platinum anodes than with platinised anodes. The increase further grew with rising temperature and increasing current density. The polarisation was further more marked when the concentration ratio $C_{OH'}/C_{I'}$ of the alkaline solution was increased.

The temperature influence upon the anode potential, as well as the difference in the potentials with smooth and with platinised platinum, can be seen from Fig. 5. The anode potentials are plotted against the electricity quantities expended, measured with a current intensity of 1 ampere and with smooth and platinised platinum at different temperatures in a solution which was normal as to KI and 0·9 normal as to iodine. The full curves refer to platinised platinum, the dotted curves to smooth platinum. We see that the polarisation is much stronger with the smooth platinum, and further that a

* *Zschr. Elektrochem.*, 16, p. 321 (1910).

† F. Herrschel, *Dissertation*, Leipzig, 1912.

rise of temperature calls forth a material increase in the polarisation. That the marked temporary rise in the polarisation, also with the iodine discharge, was indeed due to an oxygen charge on the anode, was proved by the comparison between the polarisation of a kathodically pre-polarised platinised electrode free from oxygen and the polarisation of an anodically polarised electrode charged with oxygen. The result of one of these experiments, performed with a solution normal as to KI, 0·9 normal as to iodine, at ordinary temperature, is reproduced in Fig. 6. We see at once how great the increase in the polarisation is which has been produced by charging the anode with oxygen.

The experiments alluded to leave no more doubt that the retardations, which occur when bromine and iodine are discharged from neutral or alkaline solutions of bromide or iodide, are to be traced back to an oxygen charge on the anode. When looking for an explanation of this interesting phenomenon we shall first have to consider the process of the oxygen evolution carefully.

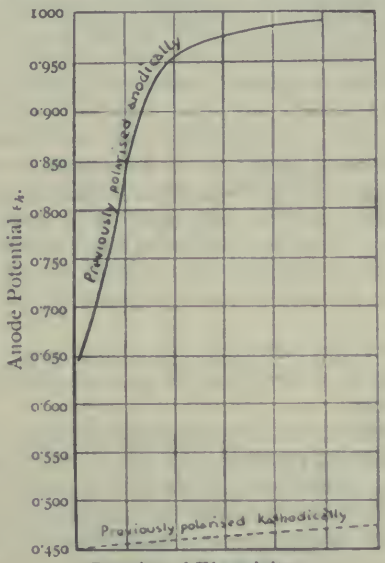


FIG. 6.

This evolution, it has long been known, does not represent a reversible process. Whilst we should expect the evolution to take place in 2N-H_2SO_4 at a potential $\varepsilon_A = +1{\cdot}23$ volt, it is so much retarded that, at a platinised anode, it does not set in before $\varepsilon_A = +1{\cdot}5$ volts, and the potentials have further to be raised when the evolution is continued. Thus the oxygen evolution shows, like the discharge of the halogens, a temporary strong rise of the polarisation value. To understand this retardation of the anodic oxygen liberation we must assume, following F. Foerster's theory,* that the potential of the electrode depends upon the anodically discharged oxygen which forms an unstable primary oxide, PtO_n, with the platinum. This oxide is soluble in the finely distributed platinum of the platinised electrode, and passes, under evolution of oxygen, into a more stable lower oxide, PtO_2 perhaps. The latter is again soluble in the finely distributed platinum. We have now to assume that the rate of decomposition of the primary oxide is

* *Zschr. Physik. Chem.*, 69, p. 236 (1909).

diminished in the same measure as the concentration of the stable oxide on the surface of the electrode increases. In order then to maintain a constant current density, *i.e.*, in order always to evolve the same amount of oxygen, the concentration of the primary oxide, and therefore the anode potential, should increase together with increasing formation of the stable oxide on the surface of the electrode. I have been able to demonstrate,* by comparative potential measurements of the platinum oxides and of platinised platinum electrodes (after polarisation in sulphuric acid), that the anodic evolution of oxygen from platinised electrodes, so far as it takes place below the anode potential $\varepsilon_A = +1{\cdot}6$ volt, is connected with the formation and decomposition of the platinum trioxide, so that PtO_3 would agree with PtO_2. For still higher potentials, observed at platinised electrodes, we must, in order to account for the oxygen evolution, presume the intermediation of a still higher oxide, possibly PtO_4.

After our having thus experimentally demonstrated that the retardation of the anodic oxygen evolution can satisfactorily be explained by the existence of unstable platinum oxides, it would appear plausible that the retarded halogen discharge from platinum electrodes could be accounted for by the aid of intermediate compounds similar to the primary oxides of platinum. Luther and Brislee† already supposed that the discharge of chlorine from smooth platinum might be secondary, *via* some unknown intermediate product lying between Cl' and Cl_2. If we accept the existence of such a product, by ascribing to platinum a certain solubility for discharged halogen ions, we might imagine that the decomposition of unstable products (which are characteristic for the *status nascendi* of the halogens) might be impeded by an oxygen charge on the anode in a similar way as we assumed for the decomposition of the primary oxides of platinum (characteristic for the *status nascendi* of oxygen).

When we review the researches which we have been discussing with regard to their bearing on the theory of passivity, the following main points should be accentuated :

1. It has been proved that the kathodic deposition of the iron metals—in itself a slowly-progressing reaction—can still more be retarded to a considerable extent by the simultaneous deposition of zinc or of hydrogen. The cause of these retardations is probably to be found in a change of the surface of the electrode, the change being characterised by the formation of unstable intermediate products of higher electrolytic solution pressure than the pure metals possess.

2. The circumstance that kathodic processes can materially be retarded by the occurrence of small quantities of foreign substances on the electrode lends essential support to the assumption that anodic processes may likewise be retarded by the formation of oxygen alloys on the anodes. In many cases therefore the cause of the anodic passivity will not be a mechanical closure (covering up) of the electrode surface by an oxide film, but the formation of an alloy consisting of the material of the anode surface and of oxygen, this alloy having a lower electrolytic solution pressure than the pure metal.

3. In the electrolytic oxidation of ferropotassium cyanide to ferripotassium cyanide a strong polarisation was always observed when the electrodes were surrounded by films of ferrocyanide or of oxides. These strong polarisations were not found with platinum, gold, nickel, cobalt, and copper in alkaline solutions. It may therefore be concluded that, in this

* G. Grube, *Zschr. Elektrochem.*, 16, p. 621 (1910).
† *Loc. cit.*

latter case, the passivity is caused, not by an oxide film, but by an oxygen alloy on the anode.

4. It has been shown that the retardations observed in the anodic discharge of the halogens are likewise to be ascribed to alloys of the platinum anodes with oxygen.

5. It has been exemplified by the anodic evolution of oxygen what we have to understand by the passivating oxygen alloys. We may imagine that the oxygen combines to a small extent with the anode material to form oxides, which in their turn form, together with the unchanged electrode material, solid solutions, and therefore one-phase systems of continuously variable composition and likewise variable electrolytic solution pressure. The oxide-film theory contrasts with this view, since according to that theory the oxide formed would mechanically cover and shut off the electrode surface so that oxide-film and electrode would form a two-phase system. The oxygen-alloy theory of the passivity thus seeks the cause of the passivity in a change of the chemical properties of the anode material, whilst the oxide-film theory finds the cause in a change of the mechanical properties of the electrode surface.

REVIEW AND INTERPRETATION OF RECENT EXPERIMENTS WHICH EXTEND AND ELUCIDATE THE DOMAIN OF THE PASSIVITY OF METALS.

(Translated from the German.)

Dr. G. Reichinstein (Zürich), who was prevented by indisposition from attending the meeting, communicated a "Review and Interpretation of Recent Experiments which Extend and Elucidate the Domain of the Passivity of Metals."

1. *Historical.*—Faraday * ascribes the discovery of the passivity to Keir,† who observed in 1790 that iron was not attacked in strong nitric acid, but assumed a "changed" state.

The problem was, however, investigated only in the thirties of the last century by Faraday and by Schönbein; the latter introduced the term "passivity." The difference of opinion between the two originators of the problem is of high historical interest. Faraday's views as to the nature of passivity were interpreted by Schönbein ‡ to the effect as if Faraday saw the cause of the passive behaviour of a metal in the formation of a well-developed oxide on the metallic surface, and Faraday is still frequently being called the originator of the oxide theory of passivity. In my opinion Faraday may with equal right be regarded as the originator both of the oxide theory and of the most modern theories of gas charges and metal-oxygen alloys; and in this sense I regard the theory which I am going to present merely as a logical consequence of the views of Faraday.

In support of this statement I quote the beginning of a letter which Faraday addressed to R. Taylor § on January 21, 1837: "Dear Sir,—I am much obliged to you for a sight of Mr. Schoenbein's paper, the experiments and observations in which are excellent. The cause of the phænomena he has so well distinguished is indeed exceedingly difficult to be distinguished at present, and I was in hopes that the doubt on my mind when I ventured the view referred to would be evident from my words. My strong impression is," etc. (*Phil. Mag.*, vol. ix., p. 61, 1836). "Moreover, Mr. Schoenbein and also M. Alb. Mousson, in an attempt which he has made to explain the cause (*Bibliothèque Universelle de Genève*, 1836, p. 165), have not given my view clearly. I have said that my impression is that the surface of the metal is oxidized, or else that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation, meaning by that, not an actual oxidation, but a relation. . . ."

Faraday further alludes to the researches of Nobili on the colours of thin plates, and he expresses the view that the latter went much further still in the opinion that skins of oxygen and acid may lastingly adhere to the surfaces of

* Faraday, Letter to Brayley, July 8, 1836, *Lond. and Edinb. Phil. Mag.*, 1836, vol. ix., p. 122.

† Keir, *Phil. Trans.*, 1790, pp. 374 and 379.

‡ Schönbein, *Pogg. Ann.*, **37**, p. 390; **38**, p. 444; **39**, p. 342.

§ *Phil. Mag.*, vol. x., p. 175, 1837.

platinum, iron, and steel without entering into chemical combination with the metal.

The above quoted letter by Faraday to Taylor further contains, near its end, the following words: "And my opinion of the cause of the phænomena as due to a relation of the superficial particles of the iron to oxygen. . . ."

From these views of Faraday has arisen the oxide theory of passivity which has been advocated up to the most recent days.*

The theory which I am going to develop is further connected with the views of M. Le Blanc,† who first expressed the idea that it is velocity phenomena which condition passivity. This assumption has successfully been developed and specialized by Fredenhagen,‡ who makes the occurrence of passivity dependent upon "a coherent, uniform gas charge"; finally Muthmann and Fraunberger § have recognized that this gas charge has the character of an alloy.

The question now, which I put to myself, and which is not discussed by any of the actual theories, is how the transition is taking place from the active state of a metal into the passive state. This question is to receive an answer which can quantitatively be tested by calculations.

Before we pass to the discussion of this question, however, we have to acquaint ourselves with a series of experiments of the very latest dates, some of which have extended the domain of passive phenomena, while others are able to introduce us into the labyrinth of passivity.

2. *Chemical Polarization of Reversible Active Metallic Electrodes.*—Before the year 1910 all the metals were distinguished as active and passive, and if there was a tendency to look for the cause of passivity in slowly progressing chemical reactions, *i.e.*, in a slow rate of ion-formation, people held on the other side that with active metals anodically treated the formation of ions took place with infinite velocity, and that any polarization observed with active metals had to be designated a concentration polarization or a diffusion polarization, that is to say, a polarization which arose owing to the differences in the concentration of the electrolyte caused by the current flow, whilst diffusion tended to balance this difference in concentration.

I should like to emphasize in this place already that these definitions of chemical or of concentration polarization are inappropriate, and that they fail in complicated cases. For the occurrence of concentration differences is not characteristic for the diffusion polarization. With one and the same electrode different polarizations are observed, always as results of different concentrations of the substances in question. The point is rather, which process is opposing the differences in concentrations to which the electric current gives rise, *i.e.*, whether this compensation is of a chemical nature or a diffusion phenomenon. Hence it would, in my opinion, be appropriate to introduce a definition like the following: If in any observed polarization the substitution of a real process by an imaginary *chemical* process, proceeding at infinite velocity, would make the polarization vanish, we should have to deal with a *chemical polarization*; if a *diffusion* proceeding at infinite rate should have the same effect, we should have to deal with a *diffusion polarization*.

Now Le Blanc ‖ described in 1910 some experiments which have revolu-

* *E.g.*, by F. Haber and F. Goldschmidt, *Zschr. Elektrochem.*, **12**, p. 49, 1906.

† M. Le Blanc, *Zschr. Elektrochem.*, **6**, p. 476, 1900.

‡ Fredenhagen, *Zschr. Elektrochem.*, **11**, p. 857, and *loc. cit.*

§ Muthmann and Fraunberger, *Sitzber. Bayer. Akad. Wissensch., München: Math.-Phys. Kl.*, 1904, p. 236.

‖ M. Le Blanc, *Die elektromotorischen Kräfte der Polarisation*, Halle, 1910, W. Knapp.

tionized our conception of active and passive metals. Two proofs can be adduced that there is only a quantitative, not a qualitative, difference between active and passive metals and that there is, in active metals, a possibility not only of a diffusion polarization, but also of a chemical polarization.

These are the proofs:

In 1904 Thatcher observed that when quite small quantities of so-called poisons are added to an electrode, at which an electrolytic oxidation is taking place, the anode potential rises considerably, which indicates that slowly progressing chemical reactions are at play. Le Blanc and his assistants now demonstrated that an addition of poisons to the active electrode Cu | $CuSO_4$ called forth the same effect. Thus 1 cm.³ of a faintly acid solution of brucine sulphate (of 1 per cent.), added to 100 cm.³ of a solution of $1N\text{–}CuSO_4 + 1N\text{–}H_2SO_4$, raises the kathodic polarization from 29 to 148, and the anodic from 14 to 40 millivolts. Strychnine raised the kathode polarization by 115, the anode polarization by 18 millivolts, etc.

When we further compare the polarizations of two electrodes under conditions, as equal as possible, of temperature, current density, concentration of the ions, etc., and when we consider that the diffusion rates must, under those equal conditions, be of the same order of magnitude, we are entitled to conclude that large differences in the polarization values of the two electrodes can only arise owing to the chemical polarization of that electrode which possesses the higher polarization value.

Thus the system Hg | $0{\cdot}1N\text{–}HgNO_3 + 1N\text{–}HNO_3$ | Hg gave, at a current density of 0·09 amp./cm.², a polarization of about 6 millivolts, whilst under the same conditions the system Cu | $1N\text{–}CuSO_4 + 1N\text{–}H_2SO_4$ | Cu gave, with electrodes of Cu quenched in methyl alcohol, 30 millivolts, and with Cu electrodes polished with emery 110 millivolts. Still higher polarizations, of the order of 500 millivolts, were obtained with the system—

$$Fe \mid 1N\text{–}FeCl_2 + 1N\text{–}HCl \mid Fe.$$

The third proof for the existence of the chemical polarization of active electrodes was given by Haber and Zawadzki* in 1912, in a paper on the polarization of solid electrolytes. They found that "solid silver salts show, with a silver anode, a polarization which increases considerably with falling temperature and which, in the case of silver sulphate, becomes so pronounced at the temperature of solid carbon dioxide, that the silver anode behaves like an anode of platinum or graphite."

A further proof for the existence of the chemical polarization of active electrodes is afforded by the fact that additions of free sulphuric acid and of its salts to the Cu | $CuSO_4$ electrode much increase the kathodic polarization.† In order to keep the effect of an addition of a neutral salt quantitatively reproducible, the electrolyte should possess a certain minimum of $H^{\cdot}$ ions; for below a certain $H^{\cdot}$ ion concentration the kathodic current intensity-potential curve of the Cu | $CuSO_4$ electrode takes a qualitatively quite different course from the curve found above this minimum. That indicates that it is purely chemical processes which are responsible for the current intensity-potential curve. Since now all the neutral salts as well as the sulphuric acid itself have the same effect, the increased polarization is evidently due to the fact that the addition diminishes the concentration of the Cu ions in the electrolyte.

* Haber and Zawadzki, *Zschr. Physik. Chem.*, **78**, p. 241, 1912.

† R. Goebel, *Dissertation*, Dresden, 1912 (researches carried out under F. Foerster). Also D. Reichinstein, *Zschr. Electrochem.*, 19, p. 520, 1913, and D. Reichinstein and A. Zieren, ibid., p. 530. These two accounts do not yet contain the results of all the experiments made.

What kind of a polarization is this then—a chemical or a diffusion polarization?

The first-mentioned case must not be confounded with another, in which the electrolyte contains the same small concentration of $Cu^{\cdot\cdot}$ ions, but in which the neutral salt and the noteworthy concentration of undissociated $CuSO_4$ are missing in the electrolyte.

In contrast to this simple case the more complicated case may be discussed as follows: Imagine an ideal case, in which the Cu electrode has a considerable concentration of the Cu ions (a), the required minimum of $H^{\cdot}$ ions, and a very small concentration (practically none) of undissociated $CuSO_4$ molecules. At a certain current density at which the kathodic polarization is still zero, a large amount of some alkali salt is added to the electrolyte, in order to reduce the concentration of the Cu ions to $\frac{a}{10}$, *e.g.*, and to set up a certain definite polarization at the same time. Let us further assume the existence of an electrode which, in the presence of the $\frac{a}{10}$ concentration of its ions (without, however, possessing the $0{\cdot}9a$ concentration of the undissociated salt) will mark, *ceteris paribus*, the same polarization as the Cu electrode referred to. The comparison between this hypothetical electrode and the really existing Cu electrode would suggest: On the one hand (case 1) the polarization of the Cu electrode would be caused by a slow (*i.e.*, secondary) transition of the ions into the metallic state; it is assumed that while the current is flowing the concentration of the ions is, by vigorous stirring, kept the same at the electrode surface as in the middle of the electrolyte. On the other hand (case 2) the polarization of the Cu electrode might be caused by the difference in the concentration near the electrode and in the middle of the electrolyte. The comparison between the Cu electrode and the hypothetical electrode now teaches: *The latter case* (2) *is only possible when the rate at which the spent Cu ions are replenished by the reaction* $CuSO_4 \longrightarrow Cu^{\cdot\cdot} + SO_4''$ *is infinitely small compared with the rate of diffusion of the Cu ions from the middle of the electrolyte to the surface of the electrode.*

The following criteria enable us to distinguish between case 1 and case 2:

If we can find an electrode such that the concentration of its ions be only $a/10$, that it contain no undissociated salt, and that it do not display any polarization, *ceteris paribus*, then that Cu electrode would belong to case 1.

If we further succeed in constructing an electrode such that, with an ion concentration of $a10$, it show *ceteris paribus* the same polarization as our Cu electrode, *but practically do not, in an electrolyte of the composition* $0{\cdot}1a$ *concentration of its ions* $+ 0{\cdot}9a$ *concentration of the undissociated salt, possess any polarization*, that would be our case 2. It should be added that case 1 represents a pure example of chemical polarization, whilst case 2 may be regarded as chemical polarization and as diffusion polarization as well. For, according to the definition formulated above, in case 2 the polarization would vanish: by substitution of the real rate of dissociation of the $CuSO_4$ by an infinitely rapid rate of dissociation, and also by substitution of the real rate of diffusion of the Cu ions by an infinitely rapid rate of diffusion.

These complicated polarization phenomena may probably be more easily investigated in practice than it would appear from this deduction; for I consider that the compensation process of case 2 will, in the predominating number of examples, practically be conditioned only by the dissociation of the undissociated salt. We shall thus either have case 1, or have case 2, in which the dissociation of an undissociated salt will represent the compensation

process. The further investigation of the Cu electrode, undertaken for the purpose of deciding the question whether the chemical polarization owes its existence to the dissociation process indicated, or perhaps to the reduction of the Cu ions (slow because of the small concentration of the latter), has suggested a solution of the problem in favour of case 1 (*loc. cit.*). This consideration is of principal importance for electrodes whose electrolytes consist of complex salts, *e.g.*, Ag | $Ag(CN)_2K$ | electrode.

Interesting examples of chemical polarization, again not due to slow diffusion of the electrolyte, can be observed when the Cu electrode is rubbed with a little mercury. These cases will be explained lower down.

In looking for an example of an electrolysis which would supply a simple analogy to the described cases of chemical polarization, that is to say, which would render clear how chemical polarization can occur with an active electrode, without the metallic electrode losing its capacity of *primarily* * furnishing ions—in looking for such an analogy (which has been found) a whole series of phenomena was recognized as exemplifying negative depolarization.

3. *Negative Depolarization.*†—What is a depolarizer? Imagine a circuit, consisting of a source of electric current having a constant e.m.f. independent of the load, and of a polarization cell, *e.g.*, of two platinum electrodes in clay cells charged with diluted sulphuric acid, these pots themselves immersed in a common beaker also filled with H_2SO_4. We close the circuit after the current intensity has reached its stationary value, and we add to the electrolyte about the kathode a solution of $CuSO_4$. Then a partly new process will set in at the kathode, and the current intensity will rise. Any material capable of producing these two effects simultaneously is usually called a depolarizer. The action of the depolarizer appears especially clear to us when it is soluble in the solvent which constitutes the electrolyte, and particularly when it does not chemically react with the electrolyte to which it is added, and does not disturb the state of this electrolyte.

Are there now such materials which, when added to the electrolyte, will not chemically react with it, and will diminish the current intensity instead of increasing it? In other words, are there any *negative* depolarizers? The reply to this question must decidedly be in the affirmative. Let the kathode of the described circuit consist, not of Pt, but of a Pd–H_2SO_4 electrode. When the electrode has, from the beginning, a small H_2 concentration, the electrolysis at not too high current densities will proceed in such a way that the whole hydrogen will be occluded by the electrode, and the polarization will be very small. We have probably to deal with a very rapid chemical compensation process constituted perhaps by the reaction between the Pd atoms and the primarily formed H atoms.

If we now add, during the electrolysis under suitable conditions, a zinc salt to the electrolyte, the polarization will increase, the current intensity in the circuit diminish, and a new process will set in: zinc is deposited on the kathode.‡

* By a primary electrochemical reaction we understand a reaction with which the passage of the current through the boundary electrode-electrolyte is connected, *e.g.*, the charging of a metallic atom with an electron, or the discharge of an ion. Since this reaction proceeds in synchronism with the electric current, it is more rapid than all chemical reactions (practically of infinite velocity). If the anodic formation of Cu ions progressed primarily, undisturbed, that would not cause any chemical polarization. The fact that chemical polarization does occur indicates that another primary reaction is proceeding, and that the $Cu^{\cdot\cdot}$ ion formation is secondary.

† Reichinstein, *Zschr. Electrochem.*, **19**, p. 520, 1913.

‡ Ibid., **16**, 1910.

The surprising feature in this phenomenon is that, of all the possible processes, it is generally the more rapid which takes place. Which means in the case of the zinc addition that that process which occurs more easily will be impeded, namely, the deposition of hydrogen from the electrolyte by the zinc which would be deposited in minimal quantities (not to be determined by weighing), even at open circuit owing to local action. The zinc hence strengthens the chemical inertia of the reaction between the Pd and H atoms, and acts as a depolarizer in a negative sense. I should like to point out in this place already that, if we desire to explain the chemical polarization of a metallic electrode—let it scarcely be recognizable or, on the other hand, sufficiently marked to lead to a generation of oxygen at the anode (= passivity) —without denying to the metallic atoms the capability of forming primary ions, then the discharge of OH′ ions, which with anodic treatment is simultaneous with the process of charging the atoms, may be regarded as the first step of a negatively depolarizing reaction. The analogy is patent ; we need only build up the mechanism of the chemical polarization in a correct way.

The behaviour of real alloys on the anode may further be recognized as an example of negative depolarization. A. Bürger and I (*loc. cit.*) have anodically investigated the alloys Cu-Ag, Cu-Hg, Cd-Hg, and Cd-Ag.

The noble metals, in amounts as small as possible, are alloyed with the surface of the baser metals. All the alloys examined have qualitatively the same property : they raise the polarization whilst the equilibrium potential remains equal to that of the unalloyed, chemically pure electrode. Thus the polarization of a Cu electrode which has been rubbed with a little mercury rises *ceteris paribus* from 33 to 161 millivolts. The anodic current density-potential curve of the alloys shows under certain conditions a point of inflection. The alloy is decomposed when the electrolysis is prolonged, and the nobler constituent aggregates or drops down from the electrode.

Of special interest for all these alloys is a strange relation between the velocity of formation of the alloy and the degree of polarization attainable with the resulting alloy. The Cu electrode may simply be amalgamated by holding it horizontally, the surface free from paraffin facing upward, and pouring some mercury on it, finally adding a few drops of concentrated nitric acid. When the electrode is quickly rinsed with distilled water, a bright mercury surface is left ; the nitric acid in this operation plays the part of the soldering liquid in the soldering process.

An electrode prepared in this way, however, hardly marks any greater polarization than the pure unamalgamated Cu electrode.

In order to prepare an electrode which will show the effect described of the amalgamated Cu electrode, every trace of HNO_3 must be avoided, and the greatest care be observed to deal with pure metals. The mercury is rubbed in the dry into the chemically pure copper surface ; this is a tedious operation, and the slower the alloy formation, the higher will afterwards be the polarization realized under anodic treatment.

To the phenomena of negative polarization might perhaps be joined another class of phenomena. In the kathodic polarization of mixtures of nickel sulphate and zinc sulphate, of the sulphates of nickel and iron and of zinc and iron, the polarization rises frequently up to the value of the baser metal, and this latter metal is likewise deposited.* These processes are not pure

* A. F. Walter von Escher, *Kathodische Vorgänge bei der Elektrolyse gemischter Lösungen von Zink- und Eisensulfat, Dissertation*, Dresden, 1912. A full literature list will be found there. Cp. also F. Foerster, "General Electrochemical Behaviour of Metals," *Zschr. Elektrochem.*, 14, p. 153, 1908.

examples of negative depolarization, however, because in the absence of the less noble metal the more noble one is deposited quantitatively, *i.e.*, with a current efficiency of 100 per cent.; at the same time hydrogen is generated. These cases are worthy of attention when one of the two metals at least in the salt mixture which is being electrolysed belongs to the kathodically passive metals.

To these experiments, which, as we shall see, introduce us into the anteroom of the passivity phenomena, others may be added, which initiate us directly into the secrets of passivity.

4. *Direct Experiments on the Passivation of Metals.*—Surprise has often been expressed at the fact that a metal turning passive does not, at higher current density, show at least that anodic solubility which belongs to it at small current density. Let a passive metal be dissolved anodically at a low current density a to the extent of 50 per cent., and let it liberate oxygen, so that its dissolution takes place at $\frac{a}{2}$ amp./cm.^{2} of metallic surface. When we increase the current intensity tenfold, the dissolution will not proceed at the rate of $5a$ amp./cm.^{2}; it does not even take place at the former rate $\frac{a}{2}$ amp., but at a much smaller rate. How is this to be interpreted chemico-kinetically? Let us assume that a passive metal Me generates primarily oxygen. Two reactions are possible:

$$(1)\ \mathrm{Me} + \mathrm{O} + 2\mathrm{H}\cdot \longrightarrow \mathrm{Me}\cdot\cdot + \mathrm{H_2O}.$$
$$(2)\ \mathrm{O} + \mathrm{O} \longrightarrow \mathrm{O_2}.$$

The commencement of reaction (2) is designated "passivity." The example teaches us that passivity is not a result of two competing reactions, for both of which the velocity would increase with increasing oxygen concentration, but: *the passivity is caused by two reactions such that the velocity of the one reaction decreases with increasing O concentration, whilst the velocity of the second reaction regularly increases with increasing O concentration.*

In 1911 I set myself the task to investigate how the rate of increase of the anodic polarization potential accompanying the flow of continuous current through a Pt-H_2SO_4 electrode differs in the two cases when the Pt electrode is free from oxygen and when it has previously been charged with O_2.* I made the following observations. A current impulse is imparted to the combination

$$\mathrm{Pt} \mid 28\%\ \mathrm{H_2SO_4} \parallel \text{clay cell-KI-I} \mid \mathrm{Pt} \qquad \longrightarrow$$

in the direction of the arrow. Its anodical amplitude is 0·1 amp./cm.^{2} of the Pt electrode, its duration 0·026 second. After the expiration of this period follows a spontaneous diminution in the electrode charge lasting 0·028 second. The rest of the anodic charge is then destroyed by short-circuiting the cell for 0·025 second. These three processes succeed one another. (The arrangement comprises a rotating commutator which closes the primary circuit, interrupts it, and closes the short-circuit; the latter could be opened and closed at will during an experiment with the aid of a cut-out.) In this way it was possible to obtain, on a photographic plate, oscillographs of the time-potential curves at open and at closed short-circuit.

At open short-circuit this time-potential curve rises steadily up to an asymptotic potential value, which is independent of the time. At closed short-circuit

* Reichinstein, *Zschr. Elektrochem.*, **17**, p. 89 (1911), and **19**, p. 672 (1913).

the curve marks a point of inflection corresponding to the moment 0·004 second after closing the circuit. This point is well marked on the oscillogram, and the experiment is easily to be reproduced. I have been able to show this with the aid of the oscillographs at different times to several scientists.

This point of inflection can only be interpreted as indicating that we have to deal with a chemical reaction, the velocity of which first increases and then decreases, as the current quantity (i.e., together with the oxygen concentration) is increasing. During a period which is smaller than 0·004 second the time-potential curve has the distinct tendency of approaching the time ordinate and a stationary value at low potentials. Every approach to a stationary condition now is connected with an increase in the velocity of the compensation process, *i.e.*, of that process in the absence of which the stationary conditions could not be reached. Now we observe a point of inflection within 0·004 second after closing the circuit, when the potential rises ; the velocity of the compensation process is beginning to fail.

Thus the curve velocity-oxygen concentration possesses a maximum.

The compensation process consists of the formation of platinum oxides (see below).

During a period which is smaller than 0·004 second, therefore, a Pt | H_2SO_4 electrode behaves, at a current density of 0·1 amp./cm.², like an inattackable electrode. The amount of Pt oxide which is formed per sq. cm., when the continuous current is not interrupted, is hence of the order of magnitude $0{\cdot}004 \cdot 0{\cdot}1/96540 = 4 \cdot 10^{-9}$ gramme-equivalent.

When afterwards the electrode is polarized for some time with the short-circuit closed, the electrode becomes covered with a yellowish layer which consists of Pt oxides. This does not occur when the short-circuit is open. We remember that platinum is dissolved with a high current yield in KCN solutions by alternating currents, but not by continuous currents. A combination, continuous currents superposed on alternating currents, is utilized in the gold industry.

A lucky accident has led us to the direct experimental recognition of the described maximum of the curve, in which the velocity is plotted as a function of the oxygen concentration.

In Russia a large amount of gold is gained by dissolving the ores in aqueous KCN solution in the presence of air as oxidizing agent. This process being very slow, there has been no lack of attempts of trying other oxidizing agents.

In this connection Andrejew* and later Michailenko and Meschterjakow† (on the instigation of Kistiakowsky) determined the rate of solution of gold in KCN in the presence of oxidizing agents. They all found that this dissolution takes place in such a manner that the rate first increases and then decreases with the concentration of the oxidizing agent. The velocity-concentration curve displays a well-marked maximum.

We may now pass to the exposition of the theories which aim at bringing all the cases of chemical polarization under one point of view.

5. *First Theory.*—The first theory was proposed at a time (1910–11) when the experiments of Le Blanc concerning the chemical polarization of active metal electrodes were already known, and when the palladium-zinc experiments were made in order to clear the matter up ; the other experiments mentioned above were not yet known, however. The theory, therefore, aimed at devising a mechanism which would admit of chemical polarization without

* J. J. Andrejew, *Journ. Russ. Phys. Chem. Soc.*, **39**, p. 1637 (1907) ; *Nachricht. Polyt. Inst., Petersburg*, **9**, p. 447 (1908) ; *Zschr. Elektrochem.*, **19**, p. 667 (1913).

† Michailenko and Meschterjakow, *Journ. Russ. Phys. Chem. Soc.*, **44**, p. 567 (1912).

denying the possibility that a system, and a passive metal-anode likewise, might primarily emit anodic ions. I should like to emphasize at this place already that this question is more satisfactorily answered by this first theory than by the second one.

The first theory* conceives a mechanism of the chemical polarization after the type of the Pd-Zn electrode. The rate of formation of the Pd-H alloy in the kathodic polarization of the Pd-H_2SO_4 electrode is given by the momentary concentration of the Pd and H atoms near the boundary of the solid electrode and of the liquid electrolyte. Let us now assume that the contact with the electrolyte at the boundary electrode/electrolyte is not formed by the solid metal, but by a solution (= alloy) of all those substances whose ions are represented in the electrolyte. The volume which this hypothetical alloy occupies in the electrode is designated the *electrode volume*.

When we add to the electrolyte of the Pd-H_2-H_2SO_4 electrode some Zn salt, some zinc will be deposited in the electrode volume already at open circuit, because the thermodynamical equilibrium demands that the potentials H_2-$H^{\cdot}$ ion and Zn-$Zn^{\cdot\cdot}$ ion must finally be equal to one another.

We now make the assumption that the zinc entering the electrode volume diminishes the concentration of the Pd atoms there. When we now treat the electrode kathodically, the rate of formation of the Pd-H alloy will be smaller, and the polarization will be greater, than before. As a consequence some more zinc will be deposited on the electrode in accordance with the higher potential. The formation of the Pd-H alloy will proceed more slowly, and the polarization will finally rise so high that zinc alone is deposited.

Analogously a Cu electrode has a certain oxygen concentration in the electrode volume already before the current is turned on. The potentials of the systems Cu-$Cu^{\cdot\cdot}$ ions and OH' ions always remain equal to one another, with or without the current flowing. That may be supposed to become possible by the splitting of the electric current into two components: two primary processes are *simultaneously* taking place at the anode—

$$(1)\quad Cu + 2F(+) \longrightarrow Cu^{\cdot\cdot}.$$

$$(2)\quad OH' + 1F(+) \longrightarrow OH.$$

Whilst the first process depresses the concentration of the Cu atoms in the electrode volume, the second process raises the O concentration there, and it is therefore the electric current which maintains the equilibrium in the electrode volume. Both the reactions increase the polarization, and the purely chemical compensation processes oppose them. The process which is subject to chemical inertia is the oxidation of the massive copper by the aid of the oxygen in the electrode volume in the presence of the H' ions of the electrolyte (any reaction between the oxygen of the electrode volume and the Cu atoms present in it is excluded, because there is equilibrium between the two systems, which, as we shall see, is a weak point of the first theory). When under special conditions the described oxidation takes place at a slow rate, the O concentration in the electrode volume and consequently the polarization rise to a high degree, until finally another compensation process sets in, for example, O_2 generation (= passivity). The equations of this theory may be deduced as follows:

Let there be: P_1, the electrolytic solution tension of the oxygen concentration in the alloy metal-oxygen, P_2, the electrolytic solution tension of its metal concentration, and p_1 and p_2 the corresponding concentrations of the ions in the electrolyte, which are assumed to be very high (= constant, prac-

* Reichinstein, *Zschr. Elektrochem.*, **17**, p. 699 (1911).

tically not variable by small current densities). When the system tends to equilibrium, only P_1 and P_2 will change, and the conditions of equilibrium will be—

$$\frac{RT}{n_1F} ln \frac{P_1}{p_1} + \frac{RT}{n_2F} ln \frac{P_2}{p_2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or—

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_1]{\frac{p_2}{P_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the most simple case where the chemical valencies n_1 and n_2 are equal we shall have—

$$P_1P_2 = p_1p_2 = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K is a constant. When we bear in mind that according to our assumption there is always (current flowing or not) equilibrium between the systems oxygen-oxygen ions and metal-metal ions, we may interpret equation (3) to mean that, when the solution tension of the metal decreases as the current flows because its concentration in the alloy is reduced, the solution tension of the oxygen must decrease at the same time. We therefore write—

$$\delta(P_1.P_2) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By differentiating (4) we obtain—

$$\frac{\delta P_1}{P_1} + \frac{\delta P_2}{P_2} = 0$$

$$-\frac{\delta P_1}{\delta P_2} = \frac{P_1}{P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If we now send the quantity of electricity 1 in the direction electrode-electrolyte, the system O-OH′ will transport the fraction r of the quantity of electricity which will discharge OH′ ions and enrich the alloy in oxygen, whilst the electricity quantity $(1-r)$ will diminish the metal concentration in the alloy. The relation between these two quantities is the following: Let the potential of the alloy with regard to the electrolyte be π during a short interval, while the current is flowing. The work to be done in order to transport the quantity of electricity 1 from the electrode to the electrolyte will be—

$$\pi = r \frac{RT}{n_1F} ln \frac{P_1}{p_1} - (1-r) \frac{RT}{n_2F} ln \frac{P_2}{p_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The ratio of the increase in the oxygen concentration to the decrease in the metal concentration of the metal-oxygen alloy may be considered equal to the ratio of these two quantities of electricity; hence—

$$-\frac{\delta P_1}{\delta P_2} = \frac{r}{1-r} = \frac{P_1}{P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and consequently—

$$r = \frac{P_1}{P_1+P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

By combining (8) with (3) we find—

$$r = \frac{K}{K+P_2^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Or in words: *When with the anodic treatment of a metal its concentration in the*

metal-oxygen alloy becomes small, then the system O-OH' will effect the whole transport of electricity : r therefore becomes equal to 1. The electrode now transports the electric current in a way, as if it were a highly noble metal ; its capability of primarily forming ions is completely suppressed, and it is limited to a secondary formation of ions.

Let us further assume that the total current in the anodic treatment of a copper electrode in the presence of $H^{\cdot}$ and of $Cu^{\cdot\cdot}$ ions of high concentration be given by the reaction—

$$2OH' + 2\oplus \longrightarrow H_2O + O.$$

We will also suppose that the slow process of chemical compensation is defined by—

$$Cu + 2H^{\cdot} + O \longrightarrow Cu^{\cdot\cdot} + H_2O.$$

Let this process be much slower than the replenishing of the OH' ions which are consumed by the current. And finally let the experimental conditions be such that the rate of percentage rise in the Cu ion concentration at the electrode within the time t is so small that it may be neglected.

If, then—

x be the total oxygen concentration which the current has supplied up to the moment t ;

x_1 that concentration of the oxygen which has chemically been bound up to the moment t by Cu and $H^{\cdot}$ ions ;

$c = x - x_1$ the oxygen concentration on the electrode surface at the moment t ;

k_o the velocity coefficient of the reaction :

$$Cu + 2H^{\cdot} + O \longrightarrow Cu^{\cdot\cdot} + H_2O.$$

i_t a variable current intensity for which the same direction is, however, always maintained ;

and if, as stated, the oxygen concentration on the electrode surface at the moment t be—

$$c = x - x_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

then the concentration at the moment $(t+dt)$ will be—

$$c + dc = x + dx - (x_1 + dx_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

According to Faraday's law

$$dx = ki_{(t)}dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where k is a proportionality factor.

The velocity of the reaction—

$$Cu + 2H^{\cdot} + O \longrightarrow Cu^{\cdot\cdot} + H_2O$$

$\left(\frac{dx_1}{dt}\right)$ is at any moment proportional only to the actual oxygen concentration because the concentration of the metallic copper is *eo ipso* constant, and the concentration of the $H^{\cdot}$ ions constant by hypothesis, and we obtain finally—

$$dc = (ki_{(t)} - k_o c)dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

from which we find—

$$c = e^{-k_o t}\left(C_1 + \int_0^t e^{k_o t} ki_t\, dt\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where C_1 is the integration constant. From the initial condition (for which $t=o$) we see at once that the integration constant is dependent only upon that oxygen concentration which corresponds to the electrode when no current is flowing. This value of c is in our case given by the equilibrium potential of the copper electrode. If we now consider that the chemical polarization of a type of electrode such as we deal with in the copper electrode will, at small current density already, assume relatively large values, which differ strongly from the equilibrium potential of the base electrode, C_1 may be regarded as infinitely small with respect to the c values, and the equation may be written in the form—

$$c = ke^{-k_0 t} \int_0^t e^{k_0 t} i_{(t)} dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This theory, which very satisfactorily characterizes the chemical polarization on condition that all the metals become primarily active as anodes, fails in many instances. Without entering into detail I will emphasize the consideration which will help us on to the right way.

We have seen that in the consideration of the anodic treatment of a metal the theory leads to quasi-secondary formation of ions, although in principle the theory starts from primary anodic formation of ions. That is just the desired result of the theory. This result is not arrived at, however, when we attempt to explain the kathodic chemical polarization by the aid of this theory. For if we imagine that the two chief components of the electrode volume consist, in the kathodic polarization of the $Cu\text{-}CuSO_4$ electrode, of Cu and of H atoms, then their quotient is constant, not their product, and the increase in the concentration of the one calls forth a simultaneous increase in the concentration of the other.

Further—and that is the chief drawback of the theory—we cannot, with its aid, come to the above-mentioned type of two reactions, of which the one is retarded by a rise in the O concentration whilst the second increases its velocity in a regular manner. This type of two reactions, we have recognized, can alone elucidate the phenomena of passivity. We can easily comprehend that we shall arrive at such a type of reaction if we imagine some reaction to take place within the electrode volume, *i.e.*, between its constituents. The first theory does not admit of that, because there is always equilibrium within the electrode volume ; and all the compensation processes of which the first theory admits are indirect reactions. In order, therefore that we may imagine a larger number of possible compensation processes, the mechanism of the electrode volume should be so designed that there should not prevail equilibrium in it while the current is flowing. The entire current must be transported by *one* system from the electrode to the electrolyte.

We also saw that the prototype of the mechanism of chemical polarization, the Pd-Zn experiment, renders it necessary to ascribe to the zinc which enters the electrode volume a diminution of the concentration of the Pd atoms. How is this to happen ? This effect is difficult to conceive if we regard the electrode volume as constant, and if we make no new hypothesis as to the mutual influences of the various constituents of the electrode volume. The simplest assumption which at once enables us to describe all the experiments mentioned is this : *The sum of the concentrations of all the constituents of the electrode volume is always constant, whether the current flows or not.*

6. *The Constant-Sum Hypothesis and the Second Theory.**—We presume

* Reichinstein, *Zschr. Elektrochem.*, 19, p. 672, 1913.

that the electrode volume is always fully saturated, and that any new constituent, possibly introduced by the electric current, ejects part of the old substances.

For the present I am not in a position to maintain the idea of a primary activity of all the systems. In view, however, of the fact that this theory satisfactorily answers all the questions concerning the chemical polarization, as well as those concerning the spontaneous solution of solid bodies in the presence of oxidizing agents, we may for the present rest satisfied with the assumption that in aqueous solutions the transport of the electric current across the boundary electrode/electrolyte is effected only by the OH' and the $H^{\cdot}$ ions.

When a metal electrode is treated anodically the oxygen introduced pushes the metal atoms out of the electrode volume—the same will happen on the kathode by the H_2 introduced—and the chemical equilibrium prevailing before the current was flowing will be destroyed. The oxygen now begins to react with the metal atoms of the electrode volume. Let this reaction be of the form :

$$Me \mid O + 2H^{\cdot} \longrightarrow Me^{\cdot\cdot} + H_2O,$$

where Me and O are respectively an atom of the metal and of the oxygen of the hypothetical alloy, and $H^{\cdot}$ concerns the electrolyte.

If the concentrations of the three substances reacting with one another are x, y, z, the velocity of the compensation process can be formulated as follows :

According to the hypothesis of the constant sum

$$x + y = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where a is a constant ; the velocity v

$$v = k_e z^2 xy = k_e z^2 y(a - y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

when, in a special case, z is a constant, the $(v - y)$ curve has a maximum. Now—

$$v = k'(ay - y^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

from which—

$$\frac{dv}{dy} = ak' - 2k'y$$

and

$$\frac{d^2v}{dy^2} = -2k'.$$

The maximum corresponds to the value $y = \frac{a}{2}$.

When with a certain current density of the electrolysis the compensation process is so rapid that the oxygen concentration of the electrode volume does not rise above the value $\frac{a}{2}$ (which we may call the *critical concentration*), then there will be no reason to fear that another compensation process will set in, *e.g.*, generation of oxygen (= passivity). When, however, the critical concentration is exceeded, the compensation process will necessarily be retarded, and the O concentration will increase rapidly until a new compensation process sets in. Instead of the above-mentioned equation of the

first theory, which defines the accumulation of the O concentration in the electrode volume after closing the circuit :

$$\frac{dy}{dt} = ki - k_o y,$$

where i is the current intensity of the continuous current, we have now—

$$\frac{dy}{dt} = ki - v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and by combining (19) and (18)—

$$\frac{dy}{dt} = ki - k'ay + k'y^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This equation gives us the above-discussed point of inflection for the y–t curve, that is to say, also for the curve which illustrates the rise of the polarization with time after closing the circuit.

We have now arrived at some point of reference enabling us to describe the experiments of Andrejew.

When we immerse a foil of gold in a solution of KCN which contains an oxidizing agent like O_2, H_2O_2 or O_3 in solution, two purely chemical reactions will come into play :

I. The formation of the gold-oxygen alloy.

This process is missing in the electrolytic dissolution of metals because in their instance the oxygen is directly supplied by the primary discharge of OH' ions, whilst here the oxygen is supplied by a chemical reaction (= decomposition of the oxidizing agent). If the oxygen were not to disappear owing to the dissolution of the gold, we should finally arrive at an equilibrium between its concentration in the electrode volume and the concentration of the oxidizing agent in the aqueous KCN solution. We may suppose that in one and the same oxidizing agent these two concentrations will bear a rectilinear relation. Now the formation of the gold-oxygen alloy, we shall see, does not proceed at an infinitely rapid rate, yet not so slowly that this process should become decisive for the entire process of solving the gold. The CN' ions are, moreover, not in contact now with the compact gold metal, but in contact with the gold-oxygen alloy, and process II is taking place.

II. $2Au \mid O\ (alloy) + H_2O + CN' \longrightarrow 2\,Au(CN)_2' + 2OH'$.

This process may, of course, proceed in several stages. When we increase the O concentration of the alloy by increasing the concentration of the oxidizing agent in the liquid phase, the critical O concentration will finally be exceeded, and the velocity of the process II will diminish more and more.

It should here be emphasized that there are many instances in which the rate of oxidation becomes smaller as the oxygen concentration is raised ; I will content myself with drawing attention to the table of these cases compiled by van't Hoff.*

The critical O concentration has now been exceeded, and, in accordance with what has been explained, a new chemical process (a second compensation process) must come into play. Such processes are the following : formation of H_2O_2 (observed by Bodländer), formation of gold peroxide.

We recognize that the occurrence of oxide layers must not be regarded as the cause of the delay in the solution of gold. The peroxide films are merely a concomitant feature, which indeed indicates that the O concentra-

* J. H. van't Hoff, *Vorlesungen über theoretische und physikalische Chemie*, No. 1, Braunschweig, 1898, p. 238.

tion of the alloy has attained high values, but which must by no means be represented as the cause of the dissolution of gold. It is a symptom, like the rise of temperature in the diseased human body.

It is interesting to note that some investigators regard as cause of the passivity that in which other investigators see the consequence of the cause of passivity.

Thus, process I supplies oxygen to the alloy metal-oxygen, and temporarily increases its concentration, whilst process II tends to diminish this concentration. In the stationary condition, when the reactions proceed at a constant rate, the concentration of the oxygen in the alloy is dependent upon the two processes I and II ; that is to say, the O concentration may be increased, not only by increasing the rate of process I, but also by diminishing the rate of process II. *Ceteris paribus*, therefore, the "critical O concentration" (in the process of dissolving gold in diluted KCN) may be exceeded with the aid of oxidation potentials of the oxidizing agents, which are so low that they would be ineffective at higher CN' ion concentration. This is in agreement with the experiments of Andrejew, according to which the characteristic film of gold peroxide appears in solutions of KCN ranging from 0·01 to 0·05 per cent., already when air acts as oxidizing agent, which demonstrates that process I is absolutely necessary. We may draw a comparison as to the spontaneous solution of passive and of active metals in the presence of oxidizing agents from this point of view. What could we predict as regards the spontaneous solution of copper and nickel in H_2SO_4 in the presence of oxidizing agents? We know that the latter of these two metals belongs to the so-called passive metals, *i.e.*, that the process of solution is slow. We should then expect, from what has been explained, that the critical O concentration of the nickel-oxygen alloy, and hence the retardation in the rate of solution of nickel, will, *ceteris paribus*, always occur at such oxidation potentials of the oxidizing agent at which this will not be attainable in the case of copper ; and it is altogether doubtful whether the v maximum will experimentally be realized in the dissolution of copper.

Of especial interest from the standpoint of the new theory are the exposition of the cases of the palladium-zinc kathode and the behaviour of the alloys mentioned on the anode.

When a palladium electrode, to the electrolyte of which a zinc salt has been added, is treated kathodically, the current is carried by the H ions. Owing to the prevailing conditions of equilibrium, some zinc will enter the electrode volume and will push out some palladium, already before the circuit is established. When the current flows, the zinc acts as ballast, because it depresses the Pd concentration according to the hypothesis of the constant sum, and hence retards the rate of the compensation process. When the concentration of the zinc in the electrode volume is γ and the sum-constant is a, the maximum of the curve, which expresses the rate of the compensation process (Pd + H reaction) as a function of the H concentration, will correspond, not to the H value $\frac{a}{2}$, but to $\frac{a-\gamma}{2}$. Now, hydrogen accumulates more and more in the electrode volume, and the polarization rises. It should be noted that the whole conception forces us to assume a chemical reaction between the H atoms and those Pd atoms which fill up the electrode volume —an assumption which was impossible according to the first theory of there being always equilibrium in the electrode volume. Thus quite generally any foreign substance entering into the electrode volume which will not take part in the compensation process may be regarded as ballast.

A special interest attaches, from this point of view, to the behaviour of the real alloys forming on the anode. When, in the case of a purely active metal, the maximum of the curve O concentration/velocity cannot be attained, that maximum can, in the case of an alloy as described, be realized, owing to the ballast, at relatively low current density, and the curve will show an inflection. An alloyed anode, therefore, displays formally the properties of a passive metal. We may imagine the whole anodic process on the following lines. As regards the space distribution the electrode, at the beginning of the anodic treatment, has the appearance : *Electrolyte|hypothetical alloy|real alloy|compact base metal.* The anodic treatment carries oxygen into the hypothetical alloy, where it partly displaces both the metals, and the chemical reaction between the oxygen and the base metal sets in. (As a matter of fact the two metals enter into competition with regard to the oxygen ; practically, however, the oxygen reacts with the less noble metal only.) The base metal, which has disappeared owing to the chemical reaction, is being replaced in the hypothetical alloy by both the metals of the real alloy. In which ratio ? That depends upon the rate of diffusion of the base metal, or upon the rate of the alloy formation of the two metals. If this rate be small, then the concentration of the base metals in the hypothetical alloy (when the current is flowing) will also be small—the velocity of the compensation process will decrease, the polarization will rise, and finally will follow the decomposition of the real alloy ; the electrode then will have the following spatial distribution : *Electrolyte|hypothetical alloy|thin layer of the noble metal|compact base metal.* The noble metal may then separate from the electrode. For this end, we know from galvanoplastic processes, a trace of impurity between the two metals will be sufficient.

In order to keep the rate of alloy formation alluded to small, we must, as has been pointed out already, exercise the greatest care as to the purity of the two metals in building up the real alloy. Certain foreign substances accelerate the alloy formation ; nitric acid in particular should here be mentioned ; it plays the part of the soldering liquid in soldering two metals.

Appendix added November, 1913.

In order further to elucidate the researches I have added a few diagrams.

Fig. 1 represents the curves current density/potential. The abscissæ are the current densities in millivolts per 5 sq. cm., the free electrode surface of my experiments amounting to 5 sq. cm., the back and edges being coated with paraffin. The electrolyte was kept well stirred during the experiments. The ordinates are the polarization values in millivolts, *i.e.*, the differences between the electromotive forces of the electrode when the current was on and when off.

The lower portion of Fig. 1 concerns Section 2 of my paper. We see that curve 1—in which case *no free* H_2SO_4 *was added to the electrolyte*—differs qualitatively from curve 2, where the electrolyte contained 0·111 gramme-equivalent of free acid per litre. When the concentration of the free acid is raised to 1·975 gramme-equivalent per litre, the polarization increases as curve 3 indicates. The same effect can be realized by diminishing the concentration of the $CuSO_4$, as curve 4 exemplifies.

The upper portion of Fig. 1 illustrates Section 3 of the paper. The anodic polarization of a pure (not alloyed) Cu electrode (curve 3) is small, and that holds still more for the anodic polarization of the Cd electrode in a solution which is highly concentrated as regards H_2SO_4 (curve 5).

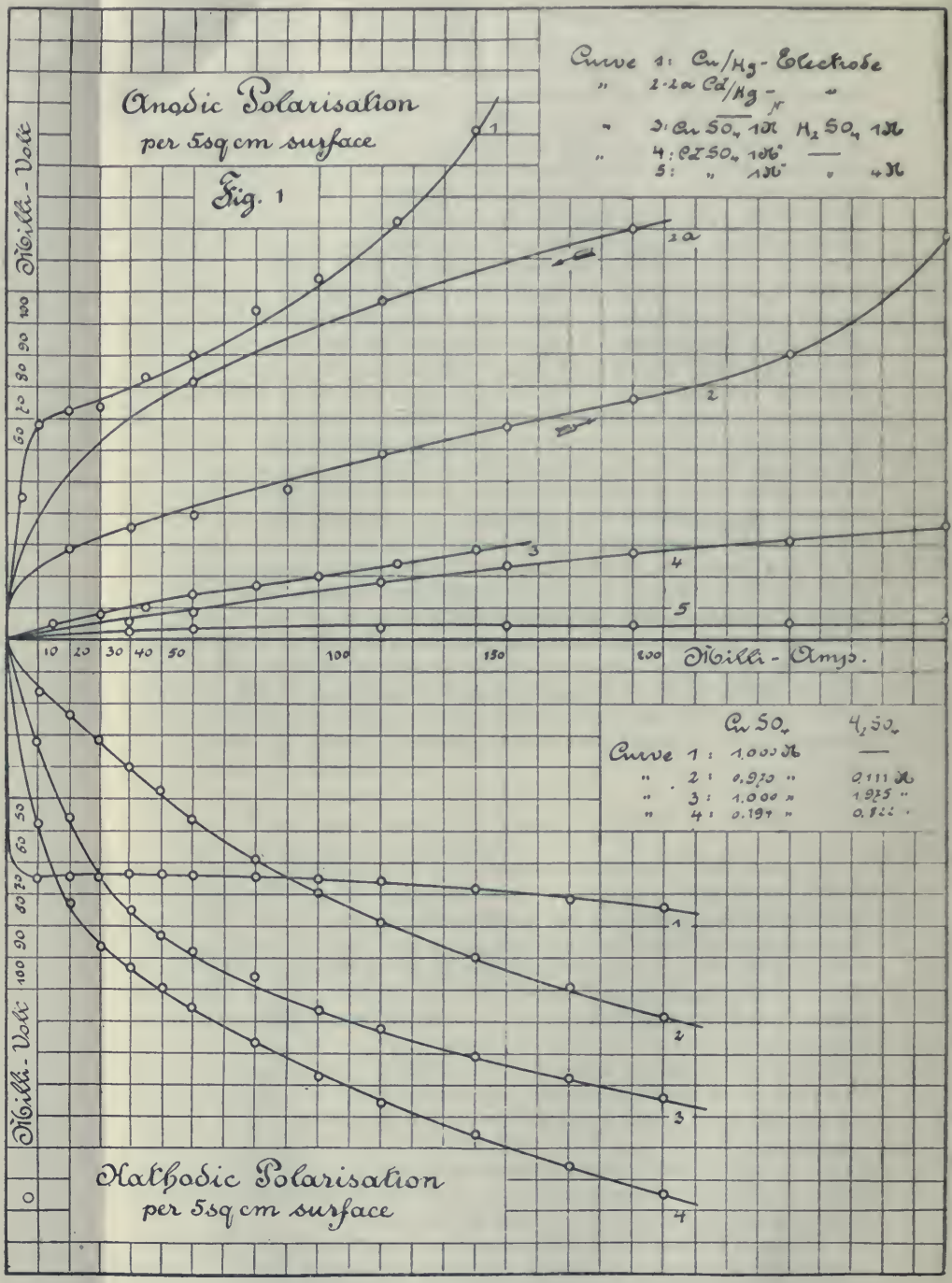

Anodic Polarisation
per 5sq cm surface
Fig. 1
Curve 1: Cu/Hg-Electrode
" 2-2a Cd/Hg- "
" 3: Cu SO4 1N H2 SO4 1N
" 4: PtSO4 1N° —
" 5: " 1N° " 4N
Millivolt-Volt
Milliamps.
Cu SO4 H2 SO4
Curve 1: 1.000 N —
" 2: 0.970 " 0.111 N
" 3: 1.000 " 1.935 "
" 4: 0.194 " 0.822 "
Kathodic Polarisation
per 5sq cm surface

FIG. 1.

As soon as we rub a little mercury into the electrode of base metal, everything changes. Curve 1 marks the polarization of the Cu electrode alloyed with Hg ; curves 2 and 2*a* refer to the Cd electrode alloyed with Hg. The experiment represented by curve 2 was made by determining the polarization value corresponding to a certain density, interrupting the current and then raising the current density after a certain interval. When finally the current density of about 350 milliamps. per 5 sq. cm. had been reached, curve 2*a* resulted when the current density was reduced again, *without, however, altogether interrupting the current.*

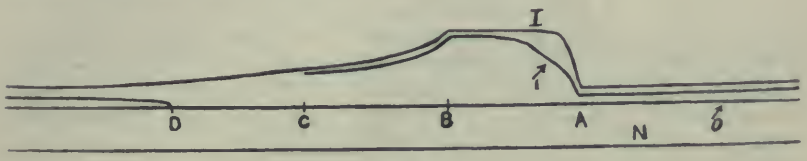


FIG. 2.

The original oscillogram, which is reproduced in Fig. 2, refers to Section 4 of the paper and illustrates the time-potential curves of two Pt electrodes in H_2SO_4, the one practically free of oxygen, and the other previously charged with oxygen. The abscissa marks the time, progressing from A to B ; 1 mm. of the abscissa is equivalent to 0·00074 second. The ordinate indicates the potential, 1 mm. being equivalent to 0·0754 volt ; o is the zero line of the oscillograph mirror, whose deflection indicates the potential ; N is the datum line. The electric circuit is closed at A and flows until the moment B is reached ; the length BC is the interval during which the electrode charge spontaneously decreases after interrupting the current ; the length CD is the

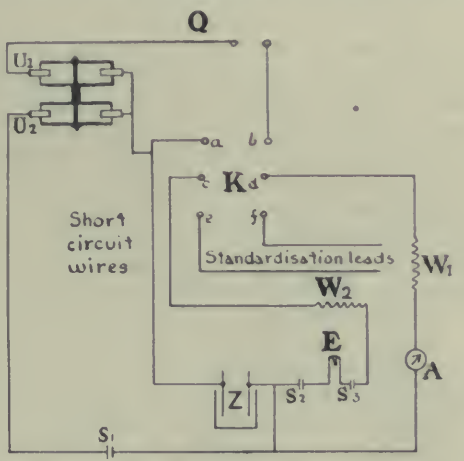


FIG. 3.

period during which the cell remains short-circuited for the purpose explained. Curve I shows the time-potential relation when the short-circuit is not worked ; curve II marks at X the point of inflection (mentioned in Section 4) observed when the cell is short-circuited in the interval CD. The resistance of the short-circuit was 2·05 ohms, that of the cell 1·40 ohms, and that of the leads for the short-circuiting 0·65 ohm.

Fig. 3 explains the general arrangement of the apparatus.

Q is a battery of accumulators ;
K a commutator ;
W_1 and W_2 are resistances, free of self-induction ;
A is a hot-wire galvanometer ;
Z is the cell under test ;
E is the sensitive loop of the oscillograph ;
S_1, S_2, S_3 are keys ;
L are the leads for standardizing the instruments.

U_1 and U_2 are two rotating interrupters, mounted on the shaft of the drum of the oscillograph and connected in the following way : When the terminals *c* and *d* of the commutator are joined to *a* and *b* and S_1 is closed, the current will flow from Q through the cell *Z*, as long as U_1 is closed ; during this period, and also for a little while after U_1 has been opened owing to the rotation of the drum, U_2 will not be in contact. As the drum continues to turn, U_2 will be closed, and the cell will be short-circuited ; during this period U_1 will, of course, be left interrupted.

THE PHOTO-ELECTRIC BEHAVIOUR OF IRON AND THE THEORY OF PASSIVITY.

Dr. H. Stanley Allen (King's College, London) read a Paper on "The Photo-electric Behaviour of Iron and the Theory of Passivity."

It is not unusual to find that investigations in one branch of science serve to throw light on problems connected with some other subject. The present research was undertaken in the hope that the study of the physical phenomenon of photo-electricity might assist in elucidating the century-old problem of the nature of "passivity." The photo-electric effect here referred to is that which is known as the Hertz-Hallwachs effect.* It consists in the loss of a negative electric charge or the acquisition of a positive electric charge by an insulated metal plate when the surface of the metal is illuminated. The experiments of J. J. Thomson and of Lenard have proved that the essential point in this electric change is the emission of negative electrons from the metal surface when the latter is exposed to light. In a high vacuum the current is carried by the electrons, in a gas the current is carried by ions formed by the association of the electron with one or more gaseous molecules. It is necessary to emphasize the fact that this separation of electrons is not the result of a chemical change, such as oxidation. The experiments of Elster and Geitel and many other investigators have shown that the photo-electric discharge takes place from the surface of the alkali metals in the highest attainable vacuum or in an atmosphere of argon or helium, and that such "photo-electric cells" retain their activity unchanged over periods of months or years. In this case the presence of a trace of oxygen would result in the formation of a layer of oxide which would effectively mask the phenomenon. The photo-electric current is due to the direct action of the electro-magnetic waves of light on the electrons of the metal; the energy of the light goes to increase the kinetic energy of the electron until the kinetic energy becomes sufficiently great to overcome the forces of attraction tending to prevent the escape of the electron.

In a paper read before the Royal Society of London I have given an account of experiments on the photo-electric behaviour of iron in the active and passive state. A polished iron plate exposed to ultra-violet light rapidly loses a negative electric charge. By finding the saturation current produced when an electric field of sufficient intensity is applied, we obtain a measure of the photo-electric activity of the metal.

Dry passive iron can be obtained by using the method described by

* We are not concerned in this paper with the photo-electric cells studied by Becquerel and Minchin, in which the potential difference between metal electrodes immersed in an electrolyte is altered by exposing one of the plates to light. Such changes may be regarded as secondary effects, while the change that we are considering is the primary photo-electric action.

Heathcote.* Experiments were made with plates of Kahlbaum's sheet iron (·2 mm. thick) and with rods of commercial iron and steel. It was found that iron which was chemically active was active in the photo-electric sense; iron rendered passive, either by the action of strong nitric acid or by use as anode in a voltameter containing dilute sulphuric acid, showed greatly reduced activity. The photo-electric activity after treatment was less than one-half of the original value, and in some cases was too small to be detected. It should, however, be noted that iron which had been rendered passive generally showed a certain amount of photo-electric activity, so that, from the point of view of photo-electricity, passive iron shows varying, though small, degrees of activity. In these experiments the chemical activity was tested in solution, using dilute nitric acid (s.g. 1·2), whilst the photo-electric activity was measured with a dry surface. Attention must be drawn to the fact that the processes employed in changing the state of the iron were all wet processes. Muthmann and Frauenberger † state that "metals become passive on lying in the air, and their potentials (in KCl solution) assume medium values, whilst vigorous mechanical cleaning of the surface renders them active." Here the reference is to chemical activity, but the statement is equally true as regards photo-electric activity. Metals exposed to the air show "photo-electric fatigue," that is to say, their activity diminishes with an increase in the time that has elapsed since they were polished, whilst repolishing the surface gives rise to a large photo-electric current.

We appear to be justified in assuming a correlation between these two sets of phenomena, and in saying that the chemical activity and the photo-electric activity vary together. If this view be correct we see that there are *degrees* of activity and also of passivity, a conclusion which appears to be in accordance with the general experience of chemists. Further, we may regard the photo-electric fatigue sometimes observed with iron as a gradual passage from the active to the passive state.

We turn now to the bearing of these results on the interpretation of passivity. In view of the resemblance between the facts connected with photo-electric activity and fatigue and those relating to the passive state of metals, it is not surprising to find that the theories advanced as to the nature of the change accompanying photo-electric fatigue ‡ correspond closely with the explanations suggested for passivity. In the table preceding the "Historical Note" these theories are given side by side.

The experiments of the author and others support the conclusion of Hallwachs that the dominant cause of fatigue is to be found in the condition of the layer of gas at the surface of the plate. So far, then, as this analogy serves, we should be inclined to attribute passivity to the surface film of gas.

We may, however, find more direct arguments in favour of the same view and against the other theories suggested.

The fact that from the photo-electric point of view different *degrees* of activity can be obtained from the same iron plate does not harmonize well with the idea of an allotropic change as the cause of chemical passivity; it agrees far better with the idea of a protective coating, whether of oxide or of gas, and best of all perhaps with the last named, *i.e.*, a gaseous film.

Byers § in a useful summary of work done on passivity points out that

* *J. Soc. Chem. Ind.*, **26**, pp. 899–917, 1907.

† *Zeit. Elektrochem.*, vol. 10, pp. 929–30, 1904.

‡ H. S. Allen, British Association Reports, 1910; *Phil. Mag.*, vol. 20, p. 572, October, 1910.

§ Byers, *Amer. Chem. Soc. Journ.*, **30**, pp. 1718–42, 1908.

"the contributors to the literature during the past ten years, with the exception of Haber and Goldschmidt, E. Müller and Spitzer, and Heathcote, unite in rejection of the Faraday view, if they fail to agree in any other particular." He regards the objections which can be urged against the existence of an oxide layer as "so convincing that we may well assent that the Faraday hypothesis may be laid to rest."

Putting on one side this view and also that which somewhat vaguely attributes passivity to the electric state of the surface, we are left to choose between the theory of an allotropic modification of the metal and the theory of the gaseous film.

Müller and Koenigsberger* found that the reflecting power of well polished iron remained unaltered when the iron was rendered passive. It was impossible to distinguish by optical means the presence of a layer of oxide, which must therefore, if present, be less than $\lambda/10$ in thickness. They support the view that passivity consists of the passage of a metallic modification of low valency into one of higher valency, but the experimental results do not seem inconsistent with the theory which attributes passivity to a gaseous film.

It has been objected to the gaseous-film theory of passivity that "a passive metal does not of necessity become active *in vacuo*.† But it must be remembered that experience has repeatedly shown the impossibility of removing films of condensed gas from the surfaces of solid bodies merely by placing them in a high vacuum.‡

If, then, we may regard the photo-electric behaviour of the metal as the criterion by which we may decide between the two principal theories, we are led to the conclusion that passivity is to be attributed to the condition of the gaseous film on the surface of the metal.

Theories of photo-electric fatigue.	*Theories of passivity.*
1. A chemical change, such as oxidation of the surface.	Formation of a protective film of oxide.
	Formation of a layer of nitride.
2. A physical change of the metal itself.	An allotropic modification of iron. "Passive" iron, trivalent; "active" iron, divalent.
3. Formation of an electrical double layer. (Lenard.)	"A permanent electric state of the surface." (Herschel.)
4. A disintegration of the metal due to the expulsion of electrons by light. (Ramsay and Spencer.)	
5. A change in the surface film of gas or in the gas occluded in the metal. (Hallwachs.)	An adherent surface film of gas which protects the iron from the action of the acid.§

Historical Note.

In the more recent literature of "passivity" the oxidation theory is rightly attributed to Faraday, but the fact that the gaseous-film theory may equally claim the authority of his name has been overlooked. Faraday in his letter

* *Phys. Zeit.*, 5, pp. 413–14, 797–8, 1904.

† H. L. Heathcote, *J. Soc. Chem. Ind.*, 26, p. 899, 1907; J. N. Friend, *The Corrosion of Iron and Steel*, pp. 190–3.

‡ Compare F. S. Spiers, *Phil. Mag.*, vol. 49, p. 40, 1900; H. S. Allen, ibid., vol. 6, p. 706, 1903; and also J. N. Friend, *The Corrosion of Iron and Steel*, chap. v.

§ An alternative form of this theory is to regard the normal state of pure iron as passive, and to attribute activity to hydrogen, probably in the ionic state.

communicating the experiments of Schoenbein to the *Philosophical Magazine* * writes: "My strong impression is that the surface of the iron is oxidized, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation."

In the August number (p. 122) he reviews some earlier observations on the *peculiar or altered* state of iron. Westlar "attributes the effect to the assumption of a negative electric state by the part immersed, the other part of the iron having assumed the *positive* state." Sir John Herschel "attributes the phænomena to a certain *permanent electric state of the surface of the metal.*" Professor Daniell suggests that the effect is due to a difference in the mechanical structure of the surface of the iron.

Thus even at this period we have representatives of the principal theories that have been advanced to account for passivity.

Schoenbein † disagrees with Faraday's view. He says: "It is evident that the different action of the same nitric acid on iron is caused by a certain electrical state of the metal." Again, "That the iron (used as electrodes in nitric acid) is not partially oxidated is evident from its unchanged metallic lustre, as also from the proportions of gas given off at both wires, which I found according to several measurements to be as 1 to 2." In the second paper he directly attacks the oxidation theory, bringing forward many objections to it, and concludes: "All the reasons above given decide me to suppose that Faraday's views concerning the passive state of the iron do not explain it satisfactorily." In the same number Faraday replies emphasizing ne guarded character of his suggestion, which need not imply an actual oxidation but "a very delicate equilibrium of forces," where there is "association without combination." He agrees with Schoenbein that a satisfactory explanation of passivity has not been reached.

Thus it will be seen that Faraday's more guarded view is essentially the same as that which attributes the effects to the peculiar condition of the gaseous film at the surface of the metal.

To sum up our conclusions, we may say that iron which is chemically active shows large photo-electric activity, while processes which render iron passive greatly reduce this activity. These facts are in good agreement with the theory, which as well as the oxidation theory must be attributed to Faraday, that the cause of passivity is to be found in the condition of the gaseous layer at the surface of the metal.

* Ser. 3, vol. 9, pp. 57–65, July, 1836.
† *Phil. Mag.*, Ser. 3, vol. 9, pp. 259–62, 1836; vol. 10, pp. 172–4, 1837.

THE PHENOMENA OF PASSIVITY.

(Translated from the German.)

A Paper by **Professor Max Le Blanc** (Leipzig) on "The Phenomena of Passivity" was read in abstract by Dr. T. Martin Lowry.

In response to the kind invitation of the Faraday Society, I take the opportunity of giving a brief survey of the phenomena of passivity, and I shall attempt to present them viewed from a uniform standpoint.

The first observations relating thereto are more remote than one usually supposes: even at the end of the eighteenth century, at the time of the discovery of galvanism, James Keir,* following on still earlier experiments by Bergman, remarked that when he poured an unsaturated solution of silver in pure colourless nitric acid upon a piece of pure iron wire, a reaction did indeed take place at first, with the separation of metallic silver; but the action of the iron upon the liquid soon ceased and the silver redissolved. Then for several weeks the iron lay at the bottom of the vessel, apparently unchanged and bright.

It is interesting to note that Keir became aware of the instability of this peculiar condition: it was lost by scratching the piece of iron, as also by touching it with a new piece.

The phenomenon was not then further investigated until 1827, when it was rediscovered by Wetzlar,† who drew attention to electrochemical relations. Fechner ‡ then made electrical measurements, which showed that by forming an element of iron-silver in a silver solution the iron remained electropositive so long as it possessed the power of dissolving spontaneously and reacting chemically. As soon as this power disappeared it became electronegative.

At the end of the thirties the investigation was continued by Schönbein,§ who published a mass of new details; especially he showed that the inactive condition of iron can be brought about by making it in a suitable manner the anode in aqueous, even dilute solutions of different oxyacids. He introduced the expression "passive," which has ever since been retained.

At this time it was known that other metals than iron could also assume this peculiar property of passivity.

Attempts to account for the phenomena of passivity have naturally been made. The discoverer himself, Keir, had thought about the matter, as can be seen from the closing words of his paper: "The explanation of these phenomena will be attempted in the subsequent paper." This promise, however, he did not fulfil.

Fechner thought of the formation of a protective coat, but the observation of the iron convinced him that it was so bright that oxidation seemed quite out of the question.

* *Phil. Trans.*, **80**, 374, 1790.
† *Schweiggers Journ. f. Chemie u. Physik*, **49**, 470; **50**, 88 and 129, 1827.
‡ Ibid., **53**, 141, 1828.
§ *Poggend. Ann.*, **37**, 390 and 590, 1836.

Faraday held a different opinion, and expressed himself thus*: "My strong impression is that the surface of the iron is oxidized, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles of the iron on the elements of successive portions of the electrolyte, and therefore not those successive chemical actions by which the electric current (which is definite in its production as well as in its action) can be continued."

This oxide theory, with numerous modifications, has been adopted up to quite recent times by a large number of investigators without any surer proof of its correctness having been brought. On the other hand, certain facts have become known which either cannot or only with difficulty can be brought into line with the theory of an oxide layer forming a protection for the electrode. Most important is the discovery of Müller and Königsberger,† according to whom the reflecting power of iron in alkaline solutions is identical in the active and in the passive state; they proved, besides, that a layer of lead peroxide of approximately molecular thickness (0·8 $\mu\mu$) deposited upon a platinum mirror greatly diminished the reflecting power of the mirror, and the optical constants of the known iron oxides and hydroxides differ only very slightly from those of lead peroxide; hence these workers both come to the conclusion that the passivity of iron is not occasioned by a coating of oxide.

Krüger‡ has recently come to the same conclusion by measuring the reflecting powers of passive and active iron for ultra-red rays.

One may object that the hypothetical oxide may have other properties than the known oxides, but one would have to confess that such an *ad hoc* supposition would be arbitrary and improbable. The same can be said of the supposition that the layer is so extremely thin that it only just covers the surface, but cannot be detected by even the most sensitive optical method. It is indeed not comprehensible on what grounds the protective layer should be formed in just such small dimensions, for in those cases in which no one doubts the formation of oxide—as, for example, in the case of the anode treatment of lead electrodes in sulphuric acid or in sodium chromate solution—the conducting metallic oxide which covers the surface after a short time becomes easily visible to the naked eye.

Such firmly adherent anodic layers, which protect the underlying metal, are always formed in electrolysis with simultaneous evolution of oxygen if the electrolyte consists simply of a salt, whose anions form with the anode metal a compound soluble with difficulty.§ Should, however, excess of another salt be added, whose anions form an easily soluble salt with the anode metal —*e.g.*, sodium chlorate in the case of lead anodes in sodium chromate solution —there is neither evolution of oxygen nor the deposition of any firmly adhering precipitate on the anode, but a precipitate is quantitatively produced, which falls away from the electrode, which remains bare. This process has been applied for the technical production of substances soluble with difficulty, such as white lead, and it is based upon the fact that in consequence of the simultaneous action of the excess of chlorate ions nearest the

* *Phil. Mag.*, **9**, 61, 1836.
† *Z. für Elektroch.*, **13**, 659, 1907; **15**, 742, 1909.
‡ *Vortrag auf der Hauptversig. der deutschen Bunsen Ges. zu Breslau*, 1913.
§ Le Blanc and Bindschedler, Isenburg, Just, *Z. f. Elektroch.*, **8**, 255, 1902; **9**, 275 and 547, 1903.

electrode a layer of liquid free from chromate ions forms soon after the commencement of the electrolysis. This layer prevents the formation of precipitate in the immediate vicinity of the electrode, and consequently also prevents any adhesion thereto.

How do *passive* electrodes behave in such cases? Nickel is passive under anodic treatment in pure potassium sulphate solution and oxygen is evolved; in pure sodium chloride solution it easily dissolves. On adding sodium chloride to the potassium sulphate solution, solution of the nickel still takes place with a moderate current density, whilst the evolution of oxygen ceases, but no detachable precipitate becomes visible. So that this observation is also unfavourable to the supposition that all cases of passivity are due to the formation of a good conducting protective layer on the electrode.

Furthermore, the strong influence of rise in temperature in restoring the activity of the metal concords ill with the oxide theory, and also the remarkable instability of this layer must excite wonder, since it finds expression in the spontaneous return of the metal to a more or less active state when the means of bringing about the passive condition are withdrawn.

This last point has already been raised by Schönbein (*loc. cit.*) as an argument against the oxide theory of Faraday. The particular passage reads thus: "A further important circumstance, to which attention must be drawn, is the fact that the iron wire, which dips in the dilute acid and remains indifferent to it, becomes attacked as soon as the electric current no longer passes through it. For instance, by leaving the wire dipping in the acid and opening the circuit in some way, there appear instantly yellowish-brown streaks shooting downwards, *i.e.*, ferric nitrate. . . . It is also clear that if the passivity of the positive iron wire be due to a film of oxide upon it, then the same wire, when removed from the circuit and placed in ordinary nitric acid, should remain passive: but this is not the case."

Thus from the various facts quoted, which can also be amplified, it is evident that the hypothesis of an impervious layer, which covers the surface of the metal, thereby protecting it from contact with the electrolyte, is open to the most serious objection.

We shall therefore attempt to arrive at an understanding of the phenomena of passivity on other grounds; this brings me to the polarization measurements for metals, immersed in their respective salt solutions, which I carried out some years ago.* Although these measurements may seem to have little to do with the problem in hand, we shall presently see that they can be brought to bear very closely upon it.

Let us take as our basis for the calculation of the potential difference at a metallic electrode Nernst's formula: $E = \frac{RT}{n_\epsilon F} \log \frac{P}{p}$ (R = gas constant; T = abs. temp.; n_ϵ = valency of the metal; F = 96,540 coulombs, P = constant for a given metal under given conditions (the electrolytic solution pressure); p = osmotic pressure of the corresponding metal ions). Let us suppose also that the formula can be applied for any desired variable condition, so long as it be reversible; then at constant temperature polarization, and consequently a rise in potential difference, can only occur in consequence of a change in value of P or of p. If we exclude the former by using a specified metal electrode, the electrode potential can only be changed by changing p, or, since p depends upon the concentration of the solution of metallic salt, simply by changing the concentration of the solution.

From this point of view we might expect that when employing a system:

* Le Blanc, *Abhandlungen d. deutschen Bunsen Ges.*, No. 3, 1910; W. Knapp, Halle-a.-S.

metal—a not too dilute solution of a metallic salt—metal (*e.g.*, copper-cupric sulphate solution-copper), no appreciable polarization would take place in the case of a short-timed electrolysis with a moderate current density, for under such circumstances no marked change of concentration of the electrolyte at the electrodes can occur. This expectation was fulfilled in the cases of the systems: lead-lead nitrate solution-lead; and mercury-mercurous nitrate solution-mercury; in all the other cases that were tried, anodic, and at the same time kathodic, polarization occurred in spite of an ample ion concentration; especially was this the case in the systems: copper-cupric sulphate or chloride in water-copper; silver-silver nitrate solution in water or in aceto-nitrile-silver; iron-ferrous chloride in water-iron; nickel-nickel chloride in water-nickel. The degree of polarization was dependent on many influences; for example, on the current density, the temperature (with rise of which it decreased), and the condition of the electrodes and solution. In many cases it could be greatly increased by addition of extremely small quantities of strychnine, brucine, gelatine, etc., and, indeed, always both at the anode and the kathode; the increase amounted to several tenths of a volt.

How can these facts be explained? Let us disregard the unlikely supposition that various obstructions oppose the processes of charging and discharging. Is there, however, not the possibility that the interchange of charge may be associated with a chemical reaction of changing velocity?

If we first consider the action at the anode, it is conceivable that primarily no metal ions are formed, as generally supposed, but that the electrical process consists of a discharge of negative ions and the chemical process of an interaction between the non-electrified radical and the metal. The potential difference would, according to this view, depend upon not only the concentration of the negative ions, but upon that of the separated non-electrified radical, and consequently upon the velocity with which the latter reacts upon the metal. For the smaller this is (*ceteris paribus*), the greater must the concentration become for a given current density, until the velocity of the reaction, which by the law of mass-action also increases, has become so great that in unit time as much of the radical disappears through chemical action as is produced by the electric current.

This view is certainly justified for series of solids, such as silver-silver sulphate or chloride-silver, which according to the researches of Haber and Zawadzki* even at low temperatures show considerable polarization at the anode; nor can any serious objection be made to its application to the series of liquids quoted above, but in the latter case we are not obliged to relinquish the usual idea of the preliminary formation of metallic ions, in order to be able to assign the observed polarization to failing chemical reaction velocity; we need only adduce the probable extensive hydration of the metal ions (or their combination with the solvent). The process of hydration which occurs at the surface of the electrode, and whose velocity depends on different influences, must then follow on the formation of ions, which, when the current passes, is practically infinitely rapid. The magnitude of the potential difference is then, it should be carefully remarked, dependent only upon the concentration of the non-hydrated, free ions, and the latter again upon the velocity of hydration. In this way polarization, which changes according to circumstances, easily explains itself—also its decrease with rising temperature, since the chemical reaction velocity increases almost without exception with rising temperature.

In a similar manner the kathodic polarization, which in these experiments always accompanies that at the anode, can be explained. The free ions must,

* *Zeitschr. f. physik. Chemie*, **78**, 228, 1911.

in the state of equilibrium, according to the law of mass-action, always be present in addition to the hydrated ones, and when the current passes they are discharged. Consequently a diminution in concentration and then polarization follows, owing to the insufficiently great speed of the formation of free from hydrated ions. Indeed, the simultaneous occurrence of polarization at the anode and the kathode finds a satisfactory explanation in this hypothesis, for both result from the same reaction: ionhydrate $\rightleftarrows$ ion + water, which takes place at both electrodes in opposite directions, and any catalytic influence, such as the quoted case of the addition of strychnine, must change the velocity of the reaction in either direction in the same proportion. Indeed, as has been pointed out, a simultaneous increase of polarization was always observed at the two electrodes.

In addition to this cause, another can be considered in the case of kathodic polarization; we may expect that the discharged metallic ion frequently does not separate as solid metal, but remains at first dissolved, forming a supersaturated solution. With increasing supersaturation polarization must increase.

The absence of polarization of the mercury and lead compounds points to the fact that in these cases the chemical and physical processes concerned take place with greater velocity.

It should be expressly understood that all the foregoing experiments were carried out under such conditions that the metals dissolve without evolution of oxygen under the action of equal currents according to Faraday's law, and further that polarization is not occasioned by any ohm-resistance at the electrodes. Were this the case, polarization would *immediately* disappear on breaking the current, whereas a gradual decline was actually observed, which could easily be followed and measured; in other words, the above-mentioned systems, which before the passage of the current possessed no e.m.f. and were unable to give a current, could do so after having first passed a current and then broken it. Hence it was proved that both at the anode and at the kathode, which could be separately examined, a condition was brought about which, at the cessation of the current, had electromotive power.*

If we account for the polarization here observed by this explanation of failing reaction velocity, we can go a step further and apply the same explanation to the phenomena of passivity. With passive metals ionic hydration occurs so slowly at the anode (a certain amount of solution nearly always takes place), that the concentration of free ions, and therefore the potential difference, becomes so great in a short time that visible separation of the negative radical or of oxygen can result. Qualitatively these phenomena present nothing new in comparison with those described before; quantitatively they are only in so far remarkable as the chemical polarization has become so strong that solution of the metal practically ceases and the negative radicals (or oxygen) are separated and become visible.

From this point of view we ought henceforth to understand by passivity phenomena all such as result from chemical polarization. We have seen that passivity is not the exception but the rule, and that it is not connected with oxygen-containing anions, as was supposed, but that it takes place also with chlorides and other solvents, and especially that it can also take place at the kathode.

* The same explanation holds for the supertension which occurs at the electrodes with liberation of gas, which also has electromotive power. I mention this because recently J. W. Richards has erroneously attempted (*Trans. Faraday Soc.*, 9, 140, 1913) to characterize this supertension merely as resistance.

Briefly it may be mentioned that one may ascribe the peculiar shift in valency which occurs on dissolving many metals, *e.g.*, chromium, by altering the experimental conditions, also to the changing hydration velocity of the ions of different valency.

I have thus attempted to establish as a fact that passivity phenomena are to be traced to those of reaction velocity. The reaction velocity theory can as yet afford no special information upon the conditions under which a metal becomes active or passive. Still one cannot reasonably regard this circumstance as a defect of the theory; it is rather due to the fact that our knowledge of the effect in chemical reaction velocities of outside factors is extraordinarily deficient. Thus another wide field is opened up for special research, and the work is being carried out with assiduity.

THE HYDROGEN THEORY OF PASSIVITY.

(Translated from the German.)

A Paper on "The Hydrogen Theory of Passivity," by **Professor G. C. Schmidt** (Münster), [experimental part by **Dr. W. Rathert**], was communicated by Dr. G. Senter.

1. *Introduction.*

Although the abnormal chemical and electrochemical behaviour of iron and certain other metals has been known for more than 100 years, up to the present no explanation of the cause of passivity has met with general acceptance. In course of time many theories have been suggested and subsequently given up. At the present time only two theories deserve serious consideration: (*a*) the oxide theory of Faraday, according to which passivity is due to a coating of oxide or oxygen on the metal—a theory which still finds supporters in spite of the many serious objections put forward against it—and the hydrogen theory, according to which the metals in question are normally passive and become active only in the presence of dissolved hydrogen acting as a catalyst. The latter view has recently been strongly supported by my pupils Grave * and Adler † on the basis of experimental investigations. Flade ‡ does not regard their results as conclusive, and considers that his own investigations lend support to the oxide theory. In the present Paper the results of further experiments designed to decide between these two theories are described.

2. *Criticism of Flade's Results.*

Flade found that iron rendered passive by anodic polarization in dilute sulphuric acid immediately returns to the active state when the polarizing e.m.f. is removed. When, however, it is in a circuit and forms the anode under the influence of an external, not too great, e.m.f., the potential gradually becomes more negative, until at a certain potential, the "transition point," it suddenly becomes active. Flade regards this point as the long sought limit between the active and passive states.

The arrangement used by Flade is practically identical with that of Fredenhagen, § and the question arises whether the transition point discovered by Flade is not the "activation potential" of Fredenhagen. If this should prove to be the case it follows, since Fredenhagen has shown that the "activation potential" and the "passivation potential" are quite different, that the formation of well-defined oxides is excluded. This point was first investigated.

* Grave, *Zeitsch. physikal. Chem.*, 1911, **77**, 513.
† Adler, ibid., 1912, **80**, 385.
‡ *Habilitationsschrift*, Marburg, 1910; *Zeitsch. Electrochem.* 1912, **17**, 335.
§ Fredenhagen, *Zeitsch. physikal. Chem.*, 1908, **63**, 1.

3. *Experimental Results.*

As a result of investigations which will be fully described elsewhere, it was found that the "transition point" is in fact identical with the activation potential of Fredenhagen, and, further, that in all cases the activation potential and the passivation potential are different. The transition point does not form a boundary between the active and the passive states, since iron can remain active at a potential which is much more positive (more noble) and passive at a potential much more negative than that corresponding with the transition point. Further, experiments with wires of different lengths show that the transition point has not always the same value. In fact, the determining factor in these investigations is the current density, or in other words, the amount of oxygen set free by the current. The investigations of Flade furnish evidence against the oxide theory, since, as Fredenhagen has pointed out, the activation and passivation potentials must coincide if oxides are formed. On the other hand, the results in question can readily be accounted for on the basis of the hydrogen theory. When iron is rendered passive by anodic polarization, the oxygen combines with the hydrogen diffusing through the iron towards the surface and thus retards solution of the metal. The iron remains passive as long as the oxygen is being liberated freely. As the amount of oxygen liberated falls off with diminishing current density a point is reached when it is no longer sufficient to combine with all the hydrogen. The iron becomes active at one point; hydrogen is immediately set free at this point, neighbouring regions become active as a consequence of local currents, and thus the whole surface becomes active with explosive rapidity. When the attempt is now made to reverse the condition of the metal, considerable resistance is met with on account of the considerable content of hydrogen and its high absorptive power for this gas. As the rate of liberation of oxygen increases, the potential gradually becomes more positive (nobler), the metal becoming passive at certain points: at other points solution of the metal proceeds and the evolved hydrogen tends to remove the passivity. As the current density and the consequent liberation of oxygen are further increased, more and more of the metal is rendered passive, until a point is ultimately reached at which the tendency to activity is overcome and the whole of the metal becomes passive. This change cannot proceed with the same rapidity as the converse one, on account of the strongly marked tendency of iron to remain active, and it is therefore not to be anticipated that the activation and passivation potential will coincide—a conclusion fully confirmed by experiment.

The behaviour of chromium is the converse of that of iron, the active condition in this case being the normal. Corresponding with this the transition point with evolution of hydrogen is quite sharp.

4. *The Effect of Polishing.*

Although the results of Flade and those subsequently obtained in the Münster laboratory can be explained on the hydrogen theory, they do not constitute a conclusive proof of the validity of that theory. The results described below allow, in my opinion, a definite decision between the two theories.

The guiding principle in these investigations is as follows: According to Muthmann and Frauenberger* passivity is brought about by the presence of oxygen dissolved in the metal. Flade accepts this view only as regards the action of air in causing passivity; all other passivity phenomena are ascribed

* *Sitzungsber. Kgl. Bayr. Akad.*, 1904, **24**, 201.

to the formation of oxide films on the metal. On either of these assumptions any metal the surface of which is cleaned in the entire absence of oxygen must be active, whilst according to the hydrogen theory it is to be anticipated that iron, which always contains hydrogen, would be active, and chromium and nickel, which do not contain hydrogen, would become passive.

In order to test these conclusions an apparatus was constructed in which the metals could be subjected to friction in an atmosphere of hydrogen or nitrogen and the potentials then determined at once. The gases were very carefully purified and air was completely excluded. It was found that when subjected to friction in hydrogen, chromium and nickel became rather more positive (nobler) but remained completely passive. These results show conclusively that metals may remain passive in the absence of oxygen, under circumstances in which the formation of an oxide film is impossible—results which cannot be reconciled with the oxide theory. The small differences of potential observed when metals are subjected to friction in different gases are due to adhering layers of gas. Iron, on the other hand, was always found to be active even in neutral solutions of ferrous sulphate : it is naturally a less noble metal than chromium or nickel, and, as the investigations of Belloc* and others have shown, always contains considerable amounts of hydrogen.

5. *Effect of a Hydrogen Charge on the Potential and Activity of a Metal.*

In the foregoing sections it has been proved that metals which contain no alloy with oxygen and are free from coatings of oxide can retain the passive condition, but in order to show the validity of the hydrogen theory it is further necessary to prove that dissolved hydrogen can transform metals from the passive to the active form. For this purpose metals prepared by electrolytic methods and therefore containing hydrogen were examined ; and, further, hydrogen was liberated at a point and conveyed by diffusion to other passive portions of the surface, under which circumstances the passive portions regained their activity.

As already mentioned, ordinary iron is active in ferrous sulphate solution, probably owing to the large proportion of hydrogen it contains. Electrolytic iron is also active under these conditions, showing a less noble potential than ordinary iron. The potential $\epsilon_h = -0{\cdot}66$ volt found by Muthmann and Frauenberger,† is, as shown by Richards and Behr,‡ too high ; it represents the potential of iron supersaturated with hydrogen. The value $\epsilon_h = -0{\cdot}4232$ volt obtained by us in good agreement with that given by Richards and Behr, is also that of a metal containing hydrogen. Muthmann and Frauenberger found that the potential can be made more negative (less noble) by adding more hydrogen, and it seems plausible to assume that by the withdrawal of hydrogen the potential will become more positive, and that finally the metal will become passive. These conclusions cannot be satisfactorily tested experimentally, as the amount of hydrogen in iron in any given case is not known and the gas cannot be completely removed from the metal.

The matter can, however, be tested in the case of nickel and of chromium. Ordinary nickel in nickel sulphate and chromium in dilute sulphuric acid are completely passive. On the other hand, electrolytic nickel and chromium, which are both highly charged with hydrogen, are active and go into solution with evolution of hydrogen.§ If chromium is deposited electrolytically on a

* *Ann. Chim. Phys.*, 1909, 18.

† *Loc. cit.*

‡ Richards and Behr, 1907, 58, 301.

§ According to Carveth and Curry, *J. Physical Chem.*, 1905, 9, 353, electrolytic chromium contains 250 times its volume of hydrogen.

sample of the same metal prepared by the Goldschmidt process, and which is quite inactive, the latter under the influence of the hydrogen also dissolves in dilute sulphuric acid. Our results are in entire agreement with those of Hittorf, who showed that even the minute trace of hydrogen liberated at a chromium electrode by making it a cathode for a moment renders the metal active. In my investigations just described the hydrogen which starts the reaction is contained in the electrolytic iron. The phenomena just described, at least as far as chromium and nickel are concerned, must be regarded as "experimenta crucis" in favour of the hydrogen theory. When the metals are prepared electrolytically or by reduction at a high temperature and subsequent rubbing in an atmosphere of hydrogen, they differ only in electrochemical behaviour and in the extent to which they are charged with hydrogen. The assumption that these two factors are in causal connection cannot be avoided, especially as the possibility of the formation of oxides or alloys with oxygen is excluded.

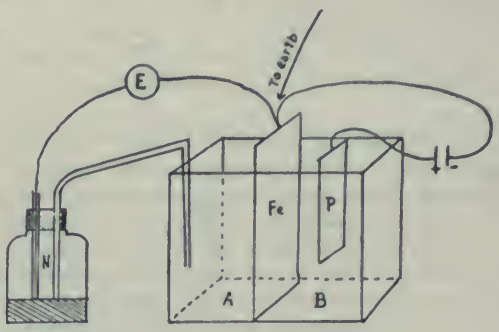


FIG. 1.

The experiments with iron are, however, not decisive, since it always remained active. The following investigations supply the evidence required:

6. *Proof that a Metal is rendered Active by Diffusion of Hydrogen Ions.—Iron.*

In order to transform passive iron into the active condition by diffusion of hydrogen, advantage was taken of the discovery of Grave* that when hydrogen is liberated at one side of a piece of iron foil, it rapidly diffuses through and alters the e.m.f. The arrangement of the apparatus was as follows: A and B are two glass troughs, one side of each having been removed and replaced by a thin sheet of iron, Fe. P is a platinum cathode connected with two accumulators. The iron is earthed. The two troughs are filled with dilute potassium hydroxide, which has a slight passivating action. N is the normal electrode. The p.d. between the iron and the normal electrode is measured by means of a sensitive Dolezalek electrometer, E. The alkali renders the metal passive, and it was anticipated that when hydrogen is liberated on one side of the iron the gas will pass through by diffusion and render the iron active. The result of an experiment is shown in Fig. 2, the times being represented as abscissæ and the e.m.f.'s as ordinates. The letters H and O indicate the moment when the liberation of these gases began. The rapidity with which the hydrogen acts is remarkable. The

* *Loc. cit.*, p. 570.

commencement of its evolution is followed almost instantly by alteration of e.m.f. on the other side.

The investigations did not, however, lead to conclusive results; the iron remained passive under all circumstances. The probable reason is that the amount of hydrogen which passes through is too small to counteract the

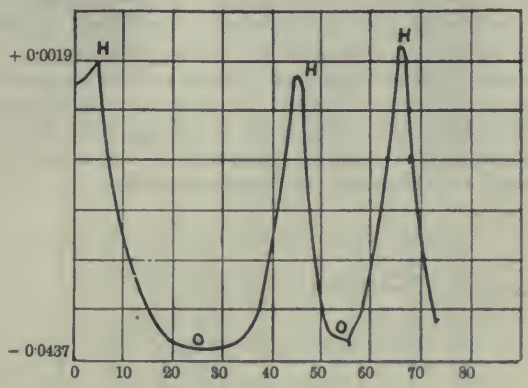


FIG. 2.

passivating action of the potassium hydroxide. The solution in the trough A was therefore replaced by another electrolyte, chromic acid. The latter is a strong oxidizing and passivating agent as well as an acid. If the hydrogen

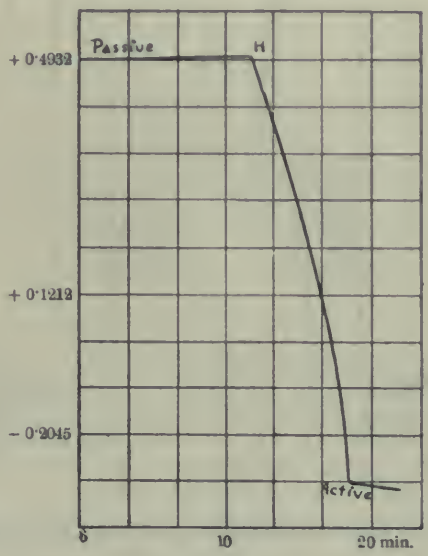


FIG. 3.

theory is correct and the iron is highly charged with hydrogen, it ought to be possible so to oppose the two properties of chromic acid that one of them prevails. Preliminary investigations showed that in chromic acid any potential through a wide range can be imparted to iron. The more concentrated the

solution the more positive (more noble) is the potential; the more dilute the solution the less noble is the potential. If an acid is chosen the concentration and oxidizing power of which is just sufficient to render the iron passive, it should be possible to render the metal active by hydrogen reaching it by diffusion. The result of such an investigation is represented in Fig. 3, which shows that the iron is at first passive, but the moment that hydrogen begins to be liberated (at H) the potential falls very rapidly and the metal becomes active. If the evolution of hydrogen is now interrupted (in the second trough B, Fig. 1) the metal remains active and dissolves with evolution of hydrogen.

Quantitative investigations showed that more iron is dissolved than corresponds with Faraday's law. This is not surprising, since iron not only goes into solution according to the law in question, but is also acted upon directly by chromic acid. This behaviour is analogous to that of a zinc electrode in

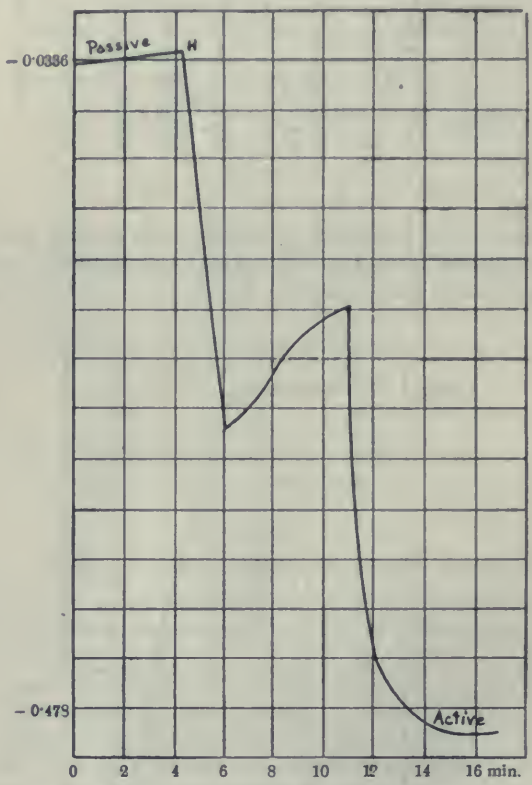


FIG. 4.

sulphuric acid; more zinc is dissolved than corresponds with Faraday's law unless the metal is protected by amalgamation against the direct attack of the acid.

These results, in combination with the above theoretical considerations, are practically conclusive in favour of the hydrogen theory. On the basis of the oxide theory, however, it might be supposed that the metal under the action of the acid becomes coated with oxide which is reduced by the hydrogen so that the electrode again becomes active. To this it might

be objected that passive iron remains quite bright in chromic acid. Further, if a layer of oxide is formed at first there would appear to be no reason why this process should not continue. This, however, is not the case, since, as was shown above, when the metal is activated by means of hydrogen it continues active even when the evolution of hydrogen is interrupted. The latter fact can readily be accounted for on the hydrogen theory as follows: When iron is in process of being dissolved and is passivated at certain points by the chromic acid, local currents are immediately set up and the passive regions again become active under the influence of the liberated hydrogen.

Moreover, according to the oxide theory, iron in chromic acid should be rendered active by rupture of the surface film by scratching, which is

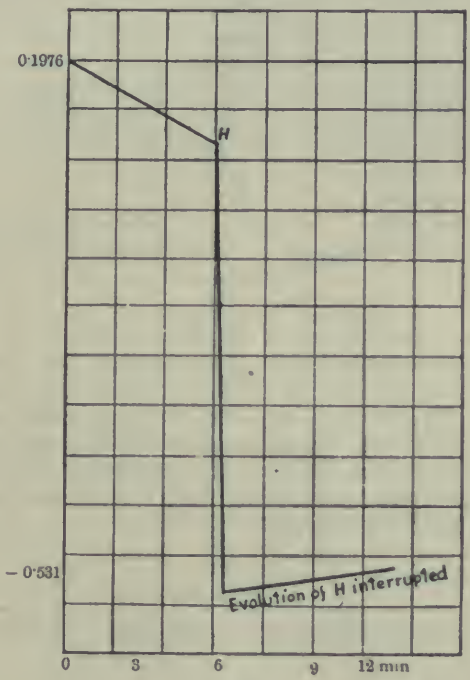


FIG. 5.

not the case. Further, an oxide of definite composition, such as is presumably postulated in this case, should show a definite potential, whilst it was found that iron in chromic acid shows all possible potentials, depending on the concentration of the acid.

All these results and arguments constitute so powerful support to the hydrogen theory as to put its validity practically beyond question, more particularly as the most delicate methods have failed to detect a trace of the hypothetical oxide.

7. *Chromium.*

The successful results obtained in the activation of passive iron by diffusing hydrogen induced me to make analogous experiments with chromium. The metal was electrolytically deposited on thin sheets of iron or steel. After about 14 days the initially active metal became passive—

probably owing to gradual loss of hydrogen. The experiments were made as described above. The results are given in the accompanying table and are represented graphically in Fig. 4.

TABLE I.

Chromium deposited on Steel and allowed to stand 14 Days exposed to the Air. Potential in 0·1 N Sulphuric Acid.

Potential.	Time.	Evolution of Gas.
	min.	
— 0·0336	0	
— 0·0262	4	
— 0·3059	6	Hydrogen
— 0·2909	7	,,
— 0·2321	9	,,
— 0·2174	11	,,
— 0·4310	12	,,
— 0·4530	13	,,
— 0·4780	14	,,

The chromium electrode was at first passive. Under the influence of the diffusing hydrogen the potential fell at first rapidly, then more gradually till it reached a value of — 0·2174 volts and finally fell within a minute to — 0·4310 volts. The electrode was then active, as shown by the fact that it began to dissolve with a vigorous evolution of hydrogen, and it continued active when the cathodic polarization was interrupted. Of the other experiments, which gave analogous results, only one is quoted, as it shows the rapidity of action of the hydrogen.

TABLE II.

Chromium deposited on a Steel Foil 0·08 mm. thick. Electrolyte 0·1 N H_2SO_4.

Potential.	Time.	Evolution of Gas.
	min.	
— 0·1976	0	
— 0·2232	3	
— 0·2488	6	
— 0·5310	6·5	Hydrogen
— 0·5310	7·5	
— 0·5246	8·5	
— 0·5112	13·5	

The results are represented in Fig. 5. The electrode was originally passive; within ½ minute of the commencement of the evolution of hydrogen it became active and began to dissolve with rapid evolution of gas. The dissolution continued after interruption of the cathodic polarization till all the chromium had disappeared.

Conclusion.

In the foregoing a series of observations have been described which in our opinion cannot be explained on the oxide theory, but are in best accord with the hydrogen theory. The views of the author on the phenomenon of passivity have already been briefly described by Grave. Just as water or other liquids do not boil, even when their vapour pressure is equal to that of the superincumbent pressure, unless a catalyst such as air is present, so the metals which can be passivated dissolve *rapidly* only in the presence of a catalyst. The most important of such catalysts is hydrogen, since it is dissolved readily and in large amount by metals. Whether other gases are also catalytically active cannot at present be stated, since they are only absorbed to a very small extent by metals. Just as relatively small amounts of air initiate rapid evaporation in large quantities of liquid, so a small quantity of hydrogen can activate large amounts of iron, nickel, and chromium. It might be supposed that the hydrogen, like air in the case of boiling, forms a nucleus round which the ions of metal collect. Further investigation must decide whether this hypothesis is in accord with the facts.

PHYSIKALISCHES INSTITUT,
MÜNSTER IN WESTPHALEN,
August, 1913.

THE RELATION OF PASSIVITY TO THE PHENOMENON OF ELECTROLYTIC VALVE ACTION.

A Paper communicated by **Professor Dr. Günther Schulze** (Physikalisch-Technische Reichsanstalt, Charlottenburg) on "The Relation of Passivity to the Phenomenon of Electrolytic Valve Action" was read in abstract by Dr. H. Borns.

Passivity and electrolytic valve action seem to be the most complicated and most difficult of explanation of all anodic phenomena. Many relations between them will be shown best by reviewing the most important features of both.

To begin with electrolytic valve action, we must differentiate between two varieties of it, ionic and the electronic valve action, the latter of which may be further divided into direct-current valve action and alternating-current valve action.

Silver in an aqueous solution of HBr gives an example of ionic valve action. If a current of $3\ \frac{\text{milliamp.}}{\text{cm.}^2}$ is passed through an anode of silver in this solution a smooth black layer is formed on the silver that grows proportional to the amount of electricity passed. After some time the colour of this layer turns to an olive-green. The formation of the layer is accompanied by a proportional rise of the electric tension across it. After a formation of some days with a current of $3\ \frac{\text{milliamp.}}{\text{cm.}^2}$ the layer attained a thickness of 0·85 millimetres, and supported a tension of 400 volts at a current density of $0{\cdot}2\ \frac{\text{milliamp.}}{\text{cm.}^2}$

The most striking phenomenon of ionic valve action, however, by which it is distinguished both from the electronic valve action and passivity, is that no gas is developed at the anode. The whole amount of current is absorbed in the formation of the solid layer. By increasing the current density it is possible to disrupt the layer, after which all the current passes through the damaged spot and gives rise to a continuous stream of gas bubbles for hours or even days, while the tension at the layer is greatly lowered. But this development of gas is only an apparent exception to the given phenomenon, as it interrupts the formation.

If the current through a formed silver anode is reversed valve action appears. The tension, high at the first moment, drops almost instantaneously to a low value. If the original direction of the current is restored the tension is low at first, but regains its former amount very quickly. These changes of tension, however, are quite unable to follow the oscillations of an alternating current of 50 periods a second, and in consequence there is not the slightest sign of rectification of such a current by a silver anode in hydrobromic acid.

It is easily understood that all these phenomena are caused by the various resistances the different ions find in the layer of silver bromide. As the time

the ions take to pass the layer is large compared to 0·01 second, ordinary alternating current cannot be rectified.

Ionic valve action occurs further with silver in HCl and HI and with copper in HF.

Electronic valve action shows quite different and much more intricate features. Aluminium, the first valve metal known, may serve as a first instance for their description.

If aluminium in a suitable electrolyte, such as a solution of $Na_2B_4O_7$, is made the anode of a constant direct current there is both oxygen developed and a solid skin of aluminium oxide formed at its surface. At first this solid skin is so extremely thin that it is invisible. After some time it appears as a whitish-grey film of a hard, almost crystalline structure that is pierced by innumerable pores of microscopic size. The formation of this solid film absorbs only about 5 per cent. of the whole current available. The rest of it develops free oxygen that escapes.

Thus the valve metals show quite the same strange phenomenon as the passive metals, viz., anodic rise of oxygen from a metal that combines with it very readily in the ordinary state.

Taking H_2SO_4 as electrolyte we find this still more obvious. Iron as well as aluminium form easily soluble compounds with it, whereas when used as anodes and loaded with a sufficient current density neither dissolve, but oxygen is set free at their surface. In the case of aluminium the phenomenon is still more puzzling than with iron, as aluminium combines very violently with oxygen. In air it only seems to be inactive because it protects itself from the oxygen by a continuous, impermeable skin of aluminium oxide, which momentarily covers every scratch made on an aluminium surface and is at first of little more than molecular thickness. By diffusion of oxygen through it, it grows very slowly. When its formation is made impossible, as by amalgamating the aluminium with mercury, a stormy reaction of the aluminium with the oxygen of the air takes place at once, and strangely shaped dendrites of aluminium oxide grow quickly and steadily out of the amalgamated surface. And for all that even nascent oxygen is set free from aluminium surfaces in H_2SO_4.

Before we try to explain this fact we must lay stress upon the most important difference between passive metals and valve metals. It is still open to discussion whether passivity is caused by a layer of oxide or not, but if there is such a layer it possesses metallic or electronic conductivity. Thus it serves as an anode instead of the metal it covers, and there is no reason why it should grow much beyond molecular thickness.

The oxide skin on the valve metals, on the contrary, insulates very perfectly. In consequence it cannot serve as an anode, but only as an obstacle that is constantly pierced by the ions and constantly regenerated by chemical action. Thus the film grows proportional to the time the current is flowing and gives rise to the following various phenomena which are completely absent from passive anodes.

The first is the rise of tension at the valve anode, that is also proportional to the time of formation until it reaches a well defined point, at which innumerable fine sparks become visible at the anode. This point is called sparking voltage. Beyond it the tension increases more slowly to a second definite value, the maximum voltage, which, with a given combination of valve metal and electrolyte, cannot be exceeded. If on the other hand not the current but the tension is kept constant at a value that lies below the maximum voltage, the current continually decreases and soon reaches extremely small values. Then the "effective layer" upon the anode has a resistance of many

megohms and may be regarded as the dielectric of an electrostatic condenser, whose conductors are formed by the valve metal on one and the electrolyte on the other side. The capacity of this condenser is easily measured and found to be surprisingly large. Furthermore, it is almost inversely proportional to the tension at which the valve metal is formed independent of the nature and concentration of the electrolyte used, as long as aqueous solutions are employed. For each valve metal, however, and every non-aqueous solvent it has a different characteristic value. One square centimetre of an aluminium anode formed at 100 volts in an aqueous solution has a capacity of 0·08 microfarads. From this capacity the thickness δ of the effective layer might be calculated if the dielectric constant ε of this layer were known. As it has not been possible yet to measure it, we must be content to calculate the relative or reduced thickness $\frac{\delta}{\varepsilon}$ by simply assuming $\varepsilon = 1$. According to the behaviour of the capacity of the effective layer stated above its thickness $\frac{\delta}{\varepsilon}$ is nearly proportional to the forming voltage and is a characteristic function of each valve metal and every non-aqueous solvent. The reduced thickness of the effective layer upon an aluminium anode formed at 100 volts in an aqueous solution amounts to 0·000010 millimetres.

At first sight it might be supposed that "effective layer" and solid oxide skin were identical, but a research as to the thickness of the latter shows that this supposition is wrong. As the oxide film is much too thin to ascertain its thickness mechanically, it must be measured in the same way as the effective layer, viz., by measuring its electrostatic capacity. The oxide film must be made the dielectric of a condenser. For this purpose it is carefully rinsed with distilled water in order to free it from the last traces of the electrolyte and carefully dried, whereupon the cell is filled with mercury instead of the electrolyte. Thus we have a condenser whose conductors are aluminium and mercury, and whose dielectric is formed by the whole thickness of oxide film. By measurements of this kind it was found that the effective layer which causes all the phenomena of the valve action and the solid oxide film are entirely different phenomena, which must be sharply distinguished. While, as stated above, the thickness of the effective layer of a given valve metal is only dependent on the forming voltage as long as aqueous solutions are used, the thickness of the solid oxide film is not only always much larger than that of the effective layer, but depends also on the nature and concentration of the electrolyte and its temperature, the density of the forming current, and may even in certain cases grow continuously, while forming voltage and thickness of the effective layer are maintained at a constant value. Thus the effective layer must be something essentially different from the oxide film, and it is hardly imaginable that it can be anything else but a gas layer within the microscopic pores of the solid film.

Thus I was led to adopt the following view of the different layers at a formed valve metal's surface and of the processes which originate it.

δ' in Fig. 1, which gives a greatly magnified diagrammatic scheme of the layers, is the whole of the solid oxide skin and consists of the following parts :—

1. α, the *continuous* oxide skin of molecular thickness that always covers aluminium surfaces.

2. β, the gas layer within the pores of the *porous* oxide film.

$\alpha+\beta=\delta$ is the "effective layer." As α is very small relative to β it may be neglected and δ simply be called the gas layer.

3. γ, the part of the solid porous film whose pores are filled with the electro-

lyte. Its resistance is a good deal larger than that of the electrolyte, but may be neglected when compared with the resistance of the gas layer.

These different layers seem to arise in the following way. If a newly polished aluminium anode is immersed in the electrolyte, it is covered with the layer α, which insulates, but for its molecular thickness can withstand only very small tensions. It is obvious that as soon as the current is closed the layer α will be pierced everywhere by the incoming ions, or rather an easily derivable part of them, the oxygen. The oxygen ions having passed the layer and reached the aluminium transfer their charge to it and form a new oxide film below the original, which is disrupted again by new ions, thus forming a thicker porous oxide skin.

But how does the gas layer form, and why does the greater part of the oxygen escape?

The only possible explanation of this seems to be the assumption that most of the oxygen ions do not reach the aluminium itself but give up their charge, the negative electrons, when they encounter an obstacle of high resist-

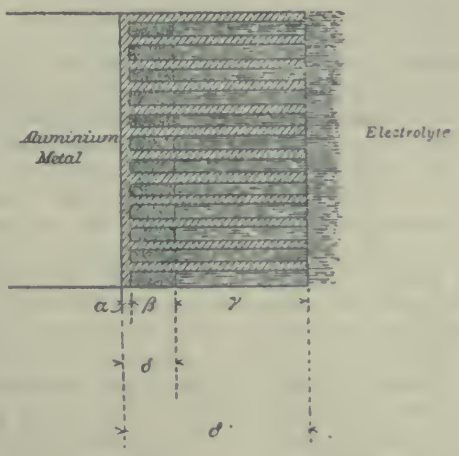


FIG. 1.

ance and in consequence a high potential gradient, and that the freed electrons only pierce the resisting layer.

The places at which the oxygen ions encounter an extremely high resistance are the junction between gas layer and electrolyte as well as the junction between gas layer and the solid continuous film α. Let us suppose that the greater part of the oxygen ions lose their electrons when they arrive at the junction between electrolyte and gas layer. The electrons fly to the aluminium and the neutralized oxygen atoms escape out of the oxide skin, as they get a heavy impact by their separation from the electrons. The small number of oxygen ions which did not give up their electrons at that limit, because the ions were just in an oscillatory state that prevented the electrons from escaping, pass the gas layer and arrive at the second junction between the gas layer and the solid film α. Here the same will happen as at the first junction. Most of the ions will lose their electrons, a few, prevented from doing so by their momentary (oscillatory) state, will pierce the solid film α, oxidize the aluminium, and reinforce the oxide film. The oxygen ions which are neutralized at this second limit cannot escape, but cause the growth of the gas layer.

It would lead us too far to show how the phenomena of valve action can be explained by means of this scheme.

Another classification of valve action, which has its analogy in passivity, is that of complete and incomplete valve action. When a valve metal is insoluble in the electrolyte it shows complete valve action. Tantalum behaves like that in almost all electrolytes. In contradistinction to it the valve action becomes more incomplete the more the valve metal is soluble in the electrolyte. Aluminium shows many instances of it. The characteristics of incomplete valve action are: the forming current does not converge to zero when the voltage is kept constant, but to a constant value, which is higher the more the valve metal is soluble. The maximum voltage cannot be reached, but the formation stops at a lower voltage. Aluminium in dilute sulphuric acid, *e.g.*, can only be formed at 20 volts instead of 400, which would be reached if the valve action were complete. The forming current must exceed a minimum value before formation sets in. After breaking the current the valve action disappears again.

Most of these features are also shown by iron becoming passive in dilute sulphuric acid, viz., a marked solubility, a minimum current for starting the passivity, its disappearing after breaking the current. On the contrary iron in concentrated HNO_3 shows complete passivity.

The performance of the valve metals as kathodes is best seen by taking oscillograms of the alternating current and voltage applied to a valve cell. As mentioned before, we must distinguish between direct-current valve action and alternating-current valve action. To which of these a cell belongs does not depend on the valve metal only but also on the electrolyte. The combinations with direct-current valve action show all the described phenomena as long as the valve metal remains anode, but the moment the current is reversed the valve action is destroyed and the cell must be re-formed from the beginning, when the valve metal is made the anode again. Alternating current is not rectified, but passes the cell unhampered in both directions.

Combinations with alternating-current valve action rectify alternating currents up to the highest frequencies. Between both there are many intermediate states. Bismuth, antimony, cadmium, and zinc are valve metals which show d.c. valve action in aqueous solutions. The reason is obvious. Their oxide films are reduced by the kathodic hydrogen. In pure sulphuric acid they rectify alternating currents, as the skin formed in this electrolyte seems to consist of the sulphate instead of the oxide and is not reduced by the hydrogen.

Here we find another relation to the behaviour of passive metals. Their passivity is also destroyed by hydrogen developed on them in the kathodic direction of the current. But this seems to be the case with all passive metals. The analogy to alternating-current valve action is missing.

This may be explained by the fact that no passive metal combines so vigorously with oxygen that the compound can withstand reduction, if the oxide-film theory is correct.

Tantalum, the *non plus ultra* of a.c. valve action, is unable to rectify alternating currents in solutions of $AuCl_3$ and $PdCl_2$, as the current in its kathodic direction deposits gold or palladium at the tantalum. To dissolve it again the same amount of electricity is wanted in the anodic direction, and the valve action is made ineffective. Other kations are only partly deposited, so that a part of the valve action survives. Fig. 2 shows this clearly. It is an oscillogram of an alternating current and voltage of the frequency 50 applied to tantalum in an aqueous solution of $Cu(NO_3)_2$, 0·2 normal; *a* is the current through the cell, *b* the tension at its connections. The surface of the tantalum was 2 cm.^{2}

At the point *o* the tantalum becomes kathode. The current remains zero until the voltage has reached the point *c* ; also in the kathodic direction there is a minimum potential that must be surpassed before the current through the effective layer can start. While it flows and deposits copper on the tantalum

FIG. 2.

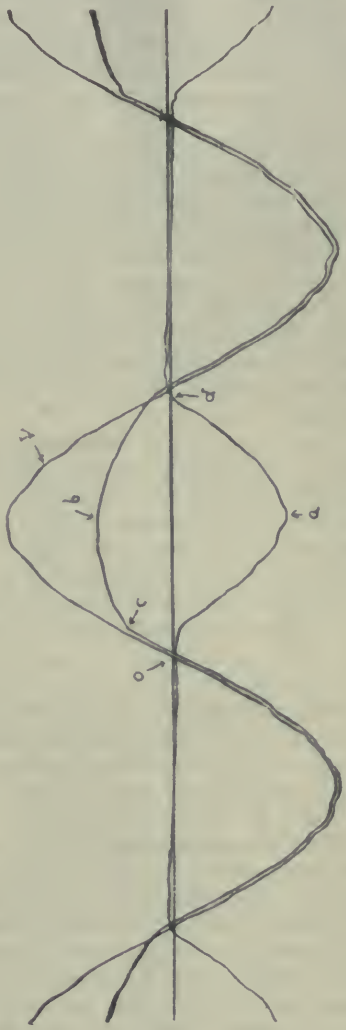


FIG. 3.

the voltage is almost constant at first, and decreases to zero, together with the current thereafter. At *d* the tantalum becomes anode ; but as there is copper deposited on it, it behaves like an ordinary copper anode up to the point *e*, where the current suddenly drops to nearly zero and the voltage rises to its normal valve value. It is obvious that when the current has reached the

point *c* all the copper deposited before on the tantalum has been consumed and the valve action is re-established. Thus only a part of the current flowing in the kathodic direction has deposited effective copper; the rest must have developed hydrogen or deposited copper in a state in which it could not serve as anode. The kations Cd, Ag, Zn, Pb, Fe, Tl act in the same way with decreasing effect along the row. With all other kations, especially with Bi, Hg, Cr, Mn, Co, Ni, tantalum shows undisturbed alternating valve action, for which the oscillogram Fig. 3 may serve as paradigma. It was taken from a cell with tantalum in an aqueous solution of KNO_3, 0·05 normal.

V is the voltage of the open circuit. The other points are easily understood on account of their likeness to Fig. 2.

The only phenomenon I want to lay stress upon is that the current *a* becomes zero at *d*, that is, before the voltage has disappeared. That proves that there is also a minimum potential below which the current cannot subsist, analogous to the electric arc for instance.

In the anodic direction the current through the cell is zero from the beginning. The small current shown in Fig. 3 does not pass the effective layer, but is the charging current of the high electrostatic capacity of the layer, as is sufficiently shown by the fact that it is shifted through 90 degrees against the voltage.

This phenomenon, that the current is zero from the beginning, is important for the theory of valve action. If valve action were caused by a partial destruction of the oxide film in the kathodic direction and a reforming of it in the anodic, as some authors formerly held, or by some kind of diffusion different in both directions, there must at all events be a re-forming current through the cell in the beginning of each anodic period. That there is none is a conclusive proof for the supposition that the effective layer is not changed by the kathodic direction of the current and that valve action cannot be explained by diffusion—in short, that it is not an ionic but an electronic phenomenon.

Summarizing the essentials of valve action from the statements above we may say: There is a defined high anodic and a defined low kathodic voltage, which must be exceeded before a current can flow through a valve electrode. The first is identical with the voltage at which the valve metal is formed, the second is the "minimum potential."

That the anodic voltage is high was explained above by the assumption that electrolytic anions must be subjected to a high potential gradient ere they lose their electrons, which in this case are bound to non-metallic atoms. In the same way the low kathodic voltage may be explained by the supposition that a relatively low potential gradient suffices to free the electrons from the valve metal. Thus the electronic valve action is caused by the different forces with which the non-metallic (electronegative) ions and metallic (electropositive) atoms bind the electrons.

The phenomena of passivity have been partly mentioned in the above. In the following only the most important of them will be summarized. Some metals which would be expected according to their position in the electrochemical series and to their general chemical behaviour to dissolve chemically in acids and anodically in electrolytes, behave differently in some cases. When dipped in certain strong acids they do not dissolve, and when made anodes in corresponding electrolytes they develop oxygen instead of forming ions. Some of them are passive in all electrolytes, others only in some cases. The latter may be subdivided into those which are passive without the aid of an anodic current and those which turn from the active into the passive

state only when the anodic current is strong enough. Iron in dilute HNO_3 or H_2SO_4 is an instance of the last type. When the iron has entered the passive state the current may be lowered a good deal below the amount at which the passivity arose before the iron become active again. Increasing temperature decreases the passivity, kathodic hydrogen destroys it.

Some authors have found that passive anodes possess a very great electrostatic capacity, and have concluded that they were covered by an oxide film. Other authors have put forward more reasons for such a film, but its existence did not remain unquestioned.

As I have not worked myself on passivity it is not for me to take a part in this controversy. The only thing I wish to point out is the remarkable analogy between the phenomena of valve action and passivity which follows from the assumption that valve action is caused by an *insulating* film and consequently a gas layer, while passivity takes place if the film shows metallic (electronic) conductivity together with a limited or negligible solubility in the electrolyte.

The consequence of the metallic conductivity of the film is that it cannot grow much above molecular size and must be almost undetectable by optical or mechanical means. The oxygen developed at its outer surface covers it more or less and protects it against the electrolyte when it has been formed. Thus the current may be decreased below the critical forming value without restoring activity.

The behaviour of iron in H_2SO_4 of different concentration is of special interest. In dilute sulphuric acid it shows passivity, in concentrated acid valve action. In intermediate concentrations an unstable valve action is succeeded by stable passivity. In dilute solutions the anion SO_4 may form an oxide of iron by the aid of the water. In concentrated solutions the small amount of water present is not available for this reaction, as it is bound to the sulphuric acid itself. Therefore ferric sulphate must be formed. This insulates and causes valve action.

Therefore I hold : Valve action is caused by an insulating skin of ultra molecular thickness with a thin gas layer within it ; passivity by a conducting skin of molecular thickness with a molecular gas layer upon it.

THE MECHANISM OF ANODIC REACTIONS AND THE BEHAVIOUR OF IRON AND NICKEL ANODES.

A Paper by **Professor E. P. Schoch** (Texas), on "The Mechanism of Anodic Reactions and the Behaviour of Iron and Steel Anodes," was read in abstract by the Secretary.

Nernst's solution tension theory assumes essentially that metal particles separate from the mass of the metal and enter the liquid direct as ions. This notion was formed from the thermodynamic expression for the electrode potential, and as thermodynamic relations are entirely independent of the "paths" through which the transformations take place, we should not be surprised to find that a study of the details of the action leads us to assume an entirely different mechanism for the electrode changes, particularly in order to harmonize our conception with our present knowledge of the properties of electrons.

The existence of free electrons in metals makes it logical and permissible to assume that when a metal is in contact with an electrolyte, electrons enter the solution and neutralize the charges on the cations in the immediate vicinity. The difference of potential thus set up between the liquid and the metal draws the anions to the latter, and on contact they react with the metal right on the surface of the latter. The resulting compounds, if soluble, then enter the solution. Similarly the action at a cathode, during electrolysis, consists of the projection of electrons *into* the electrolyte and the neutralization by these electrons of cations near the cathode. The neutralization takes place away from the cathode, and the separation of the neutral metal from the electrolyte and their deposition on the cathode is a subsequent change.

There are many facts that support the view that the neutralization of cations takes place *within* the electrolyte: we need but recall the fact that the passage of the current is hindered but slightly by gas films such as are found on metals which exhibit the phenomenon of overvoltage, and that the passage of the current is hindered but slightly by films which cover the surface of the aluminium in the electrolytic rectifier when the aluminium acts as the cathode. Again, the neutralization of the electric charges on cations while the latter are still within the liquid is indicated by the co-deposition of metals in the form of alloys, and by the observation of supersaturated *neutral metal* solutions in connection with their electrodeposition.* In the latter instance, electric discharge does not necessarily take place "at a distance" from the cathode, but in the first-mentioned instance above, gas films certainly prevent direct contact between cations and cathode. That the passage

* *Z. Elektrochem.*, 13, 1477; *Trans. Chem. Soc.*, 1907, 385: *Abh. Bunsen Ges.*, No. 3, p. 75.

of electrons from cathode to electrolyte through gas films actually takes place *readily* during electrolysis has been positively established by Günther Schulze * in his study of electrolytic rectifiers.

This modification of Nernst's original conception of cathode actions follows as a matter of course from our present knowledge of electrons and the immobility of positive electric charges. However, this does not compel any modification of Nernst's view applied to the anodic dissolution of metals ; and it is probably on this account that the notion of the direct formation of cations from metals is still adhered to more or less definitely. Even Le Blanc,† who was the first to point out that all electrode reactions take place with a finite velocity and hence involve chemical changes besides the electrical change, considered that "the usual conception of the primary formation of the metal ions" is able to account for this finite velocity if it is amplified by the idea that the *primary* cations undergo the chemical change of hydration before they are in their final form.

However, in this same publication Le Blanc states that the idea of a direct attack of the anions upon the metal anodes may also be assumed to be the course of the reaction, this chemical change determining the finite velocity. He states that at the time of the writing of that article (March, 1909) both mechanisms of anodic reaction must be admitted as equally possible, and he suggests that they may take place simultaneously, and that the conditions may make one or the other more prominent. However, he does not mention the direct "anion-metal" reaction beyond this general statement.

The notion of the direct formation of cations from metals has the vital defect of not taking into account, in any direct manner, the well-known specific effect of the particular anions present. For a striking illustration of the latter effect one need but point to the difference in the rate of the action of zinc with dilute sulphuric acid and with dilute hydrochloric acid ; or to the marked effect of the small amounts of certain anions such as the chloration, added to sulphuric acid in the Planté method of forming positive storage-cell plates. This specific effect of the anions is best accounted for by assuming a direct attack of the solid metal by the anion with the subsequent dissolution of the compound.

As the facts appear to the writer there is nothing in the behaviour of metal anodes that requires the assumption of the direct formation of cations from metals in contradistinction to the direct attack of the anode by the anions, and since the latter mechanism of the reaction must actually be assumed to take place in many cases, only this mechanism of the reaction will be considered in the remainder of the article.

This conception of anode changes takes care of the specific influence of the anions, and leads us to expect that the velocity of reaction depends upon *both* reacting components ; but before the general behaviour of anodes can be considered some other facts must be taken into account.

Günther Schulze ‡ has shown that in the electrolysis of phosphate, borate, etc., solutions with an aluminium anode, the following distinct layers are formed upon the metals : First, a very thin, non-porous layer of oxide ; second, a porous layer of oxide which becomes thicker with increasing

* *Ann. d. Phys.*, 21, 929 ; 22, 543 ; 23, 226 ; 24, 43 ; 25, 775 ; 26, 372 ; 28, 787 ; and still later papers.

† M. Le Blanc, "Die Elektromotorischen Kraefte der Polarisation, und Ihre Messung mit Hilfe des Oszillographen," *Abh. Bunsen Ges.*, No. 3. See also Reichinstein, *Z. Elektrochem.*, 16, 916 (1910), who observed polarization even in those cases in which Le Blanc observed none definitely.

‡ *Ann. d. Phys.*, 28, 789.

potential, and which is slowly but constantly reformed next to the metal as the layer next to the electrolyte is slowly dissolved ; third, oxygen gas, which fills the pores of the porous film. He also observed an evolution of oxygen gas on the surface between the film and the electrolyte. His conclusions concerning the formation of these films are the following :

1. The first, very thin, film of oxide on the metal is formed with the oxygen of the air.

2. This thin layer hinders or prevents direct access to the metal of complex anions such as sulphation, phosphation, etc., and under the stress of the potential drop through this layer, these anions dissociate, producing an equivalent number of oxygen ions which on account of their lesser bulk can pass through the oxide layer (and in passing through it perforate it) and then reach the metal surface to be discharged there. The oxygen discharged on aluminium naturally forms a new layer of aluminium oxide next to the metal, while the outer portion of this oxide layer, made porous by the passage of the oxygen ions, develops the porous layer.

3. As the oxide layer thickens, the potential fall in it becomes great enough for some of the ions to give up their electrons before they reach the electrode, thus forming oxygen gas : the passage of the free electrons through the dielectric is plainly shown by numerous fine sparks.

It is needless to follow Schulze's explanation beyond this point, because his other observations have no bearing on the question of ordinary anode actions. The following general conclusion may be drawn from his work and should be emphasized : A film, or cover, over the surface of an anode will hinder or prevent the direct access to the surface of the metal of complex anions and will bring about the formation of oxygen ions from them. The latter pass on to be discharged on the surface of the metal.

This gives us all the facts necessary for the explanation of the chemical change of any anode in any electrolyte. Briefly this explanation may be stated as follows : With a clean anode surface the anions come in direct contact with the metal, react with it, and give up their electrons : the rapidity of the reaction and the final products obtained will vary greatly with different metals and different anions. The product may be so rapidly formed and so rapidly dissolved that other anions may have unhindered access to the surface. Again, the reaction may take place slowly, or the product may dissolve slowly, or the latter may be insoluble, or it may be hydrolysed into an insoluble compound, so that other ions may find their progress to the anode more or less obstructed—a condition that may naturally be brought about in almost any case by a sufficiently great current density. Many complex ions which are prevented by the obstruction from reaching the surface of the metal will dissociate into an equivalent number of oxygen ions, which reach the surface of the metal more readily. Upon discharge these oxygen ions may form the oxide of a metal (as with copper in sulphate electrolytes), or they may form partly an oxide and partly oxygen (as with platinum in sulphate electrolytes), or they may react so slowly that the discharged oxygen still in contact with the metal becomes gradually more condensed as more oxygen ions are forced into the same area with a greater potential difference until finally gaseous oxygen, or perhaps some higher oxide of the metal, is formed.

In the absence of any "oxide skeleton" the layer of oxygen, on thickening, would soon allow bubbles of gas to escape—as is probably the case with platinum, iridium, etc., in which the oxide formed is within the body of the metal. But when a non-conducting oxide skeleton is formed the layer of gas may accumulate to a relatively great thickness as the oxide skeleton grows, and this may prevent more or less completely the passage of any ions to the

electrode.* Finally, if the oxide is oxidizable to a conducting (per-)oxide, then a suitable concentration of oxygen produced by its discharge under a sufficiently great potential will produce this peroxide, and oxygen gas will then be evolved from the new surface of the peroxide. The actual existence of this latter state of affairs has been beautifully demonstrated by E. Mueller,† who showed that a copper anode in sodium hydroxide solution forms hydrated cuprous oxide as long as the current density is small enough ; but with a larger current density the anodic potential becomes more noble, copper peroxide is visibly formed on the anode, and then oxygen is evolved from the surface of the latter. It appears that the "oxygen producing" discharge of ions on *peroxide* anodes is a rapid reaction, because no great hindrance is observed even with great current densities.

This beautiful demonstration by E. Mueller of the relations between active and passive copper indicates that the phenomena which characterize the attainment of passivity by some metals in certain electrolytes appears to be nothing but the regular behaviour of anodes under the existing conditions. The writer's study of the behaviour of iron and nickel anodes in various electrolytes has led him to the same conclusion with reference to the passivity of these metals. These facts will now be reviewed in the light of the general theory of anode actions outlined above.

Iron or nickel placed in solutions of their (neutral) salts will assume a definite "equilibrium" potential.‡

When such electrodes are used as cathodes during electrolysis *alloys* of iron or nickel with hydrogen are obtained which exhibit higher (more zincic !) potentials than the equilibrium potentials of the metals.

When such electrodes are used as anodes during electrolysis, with current densities below a certain approximate limit, then only dissolution of the metal will occur, and with any one particular current density the anodic polarization (or potential drop below the equilibrium potential) will be the same whether the particular current density is approached through a series of increasing or decreasing current densities (in the latter case even the largest current densities in the series must not have exceeded the "limit" mentioned above). In other words, current densities within this limit do not leave a "permanent" effect upon the surface of the electrode. With an electrolyte containing any one particular anion the approximate limit of these current densities which do not leave a permanent effect upon the anode is extended to greater current densities by (*a*) raising the temperature, (*b*) an increase in the concentration of the hydrogen ions or a decrease of the hydroxyl ion, (*c*) by stirring or replenishing the electrolyte on the surface of the anode. Hence the writer's experiments were made at different temperatures—most of them at 25° C., and a few at 98° C. ; the concentration of the hydrogen ion was definitely known and varied from one-tenth normal acid to one-tenth normal alkali ; and in all experiments the electrolyte was stirred vigorously and uniformly, and in the experiments with iron fresh electrolyte was also passed constantly through the anode chamber in order to avoid the complicating oxidation of the ferrous salt formed.§

The particular electrolytes employed were (*a*) neutral solutions of ferrous or nickel sulphate and chloride, solutions of potassium sulphate, nitrate, perchlorate, chlorate, bromate, iodate, chromate, hydroxide, and sodium

* However, such a film will still allow free electrons to pass from the electrode to the solution, which gives the pole the property of an electric *valve*.

† *Z. Elektrochem.*, 13, 133.

‡ *Z. Physik. Chem.*, 58, 301 ; *Am. Chem. J.*, 41, 208.

§ *J. Phys. Chem.*, 14, 739 ; *Am. Chem. J.*, 41, 235.

acetate; (*b*) acidified and alkaline solutions of the sulphates, nitrates, and acetates; and (*c*) mixtures of sulphate with chromate and sulphate with fluoride. Arranged in increasing order of their limits of the current densities with which the surfaces of iron or nickel anodes are not "permanently" affected, the anions present the following list:

(*a*) Hydroxides, iodates, bromates, chlorates, chromates, with all of which only exceedingly small current densities do not affect the surface of the anode permanently;

(*b*) Nitrates;

(*c*) Perchlorates;

(*d*) Acetates;

(*e*) Sulphates;

(*f*) Halides—with the latter large current densities do not affect the surface.

With current densities beyond such limits, the action of the current produces a *permanent* effect—that is, the effect remains for a finite period of time after the current has ceased to flow, and with the same current density an iron or a nickel pole may show widely different potentials depending on its "previous history" in an incontrollable manner. In general, it may be said that the potential of the electrode will become lower (more noble!) with the length of time that such current densities beyond the above limit continue to flow, and the potential drop will be more rapid with greater current densities than with lesser. In many cases the potential will drop almost suddenly down to the potential with which oxygen is evolved. When the surface of an electrode has been affected by electrolysis with a current density beyond the "limit" above, then an exceedingly small current density will suffice to keep its potential steady—that is, will suffice to maintain the electrode surface in the state in which it is. But when the current ceases to pass, the iron or nickel electrode immediately begins to lose its permanent effect *in all electrolytes*, and it is only a question of time until the surface is again in its original state.

These are the general facts in the behaviour of iron or nickel anodes in various electrolytes. They are readily explained by the general theory of anode action, as follows:

With current densities below the limit mentioned, the ions are discharged upon the electrodes, where they react with velocities depending on the specific relation between each anion and each metal. When the surface of the anode is covered with discharged anions which are still in process of reacting, access of other anions to the surface is impeded, and the production of oxygen ions near the electrode will begin. The discharge of the latter upon the metal surface produces the permanent effect; and anything that will delay or hinder the formation of these oxygen ions will widen the limit of the current densities which do not affect the surface. An increase of temperature, as usual, will increase the velocity of reaction between the anions and the metal, and thus lessen the time during which the reacting masses cover the electrode. Stirring will help to remove the reaction products more rapidly. An increase in the hydrogen ion concentration will lessen the tendency for the formation of oxygen ions from the other ions, so that a potential difference higher than without the acid is required to bring about the same amount of dissociation into oxygen ions. Finally, a glance at the order of the anions in the list above reveals that this also is in accord with our theoretical notions: the ions which even with small current densities permanently affect the surface are hydroxylion, iodation, bromation, chloration, chromation—the first one of which is the oxygen ion itself, and the others are just the ions which may be

expected to dissociate into free oxygen ions much more readily than the others farther down the list.

The loss of the "permanent" effect which iron or nickel electrodes experience in all electrolytes after the current ceases to pass is in the nature of a discharge of a short-circuited cell: the "oxygen" spots act as the positive poles, and the uncovered spots (which were previously occupied by the reacting anions) act as the negative poles.

It has thus been shown that the general facts observed in these experiments are explained satisfactorily by the theory of anode actions first outlined. In conclusion a few special remarks should be made in anticipation of possible objections raised to this theory or counter-claims made for other theories.

No special attempt was made to state in what particular form the oxygen obtained by the discharge of oxygen ions is present on the surface of iron or nickel anodes, that is, whether it is present as free oxygen or as oxide. To the writer there do not appear to be any facts which establish one view over the other.* The assumption of a free oxygen film is perhaps a trifle simpler than the assumption of a formation of an oxide, but the possibility of the presence of an oxide has not been disproved even by the experiments of Mueller and Koenigsberger.†

Grave ‡ has recently presented facts and arguments in support of Foerster's § suggestions that the hydrogen in iron or nickel may be the catalyser to which they owe their activity, and hence when it is more or less completely absent these metals should be relatively inactive—passive. While it is a fact that hydrogen *alloys* with hydrogen or nickel, and that these alloys show a higher potential with higher percentages of hydrogen in them, yet these alloys really present only the same general relation which other alloys and other mixtures present. In the condensed form into which the hydrogen is probably compressed by the "surface effect" of the metal, the hydrogen itself would exhibit a potential as high or slightly higher perhaps than the alloys, and hence the potentials of the alloys thus appear to be below the potential of the "higher potential component"—a relation that is shown by all alloys. Furthermore, the activity of iron or nickel is also much greater with halide electrolytes than with others, such as sulphate electrolytes, even though hydrogen ions are equally absent in both electrolytes, and the theory of the catalytic influence of hydrogen upon these metals fails to account for this.

Possibly the best experimental evidence for a decision between this hydrogen catalysis theory and the theoretical views we have here advanced is the following.

A chromium anode that has become passive with reference to the formation of bivalent ions does not become active again to form trivalent ions, but does become active again to form chromation.

An iron anode that has been made passive with reference to the formation of bivalent ions does not become active again to form trivalent ions. However, when electrolysed in acetate or oxalate solutions the electrode becomes

* *Am. Chem. J.*, 41, 251.

† *Physik. Z.*, 6, 847. These authors compare the reflecting power of two polished slabs of iron placed in sodium hydroxide solution. One of the slabs was "passivized" and then allowed to regain its normal state; and while it went through these changes its reflecting power was found to remain constant and the same as that of the slab which was not passivized. The fundamental error here is the assumption that the slab which was simply immersed was not acted upon: a slight electrolytic action undoubtedly took place between different spots of this slab, and the *difference* in the extent to which the slabs were affected is naturally much less conspicuous than the difference between a changed and an unchanged surface (and hence probably not observable).

‡ *Z. Phys. Chem.*, 77, 513. § *Abh. Bunsen Ges.*, No. 2.

active again (that is, the metal dissolves again extensively) at potentials considerably below those (more noble!) at which it had ceased to be active before and at which it is usually passive in other electrolytes. The same thing is true of nickel.*

In all three instances above the activity at the lower potential is due to a reaction which consumes oxygen and thus lays the metal surface bare. This is plainly the case in the formation of chromations. In the other examples the activity of the iron or nickel reappears when the potential is low enough to oxidize the acetion or oxalation, and when the oxygen is removed to oxidize these substances, then the metal surface is exposed and is subject to the attack of the anions.

* *J. Phys. Chem.*, 14, 719; *J. Am. Chem. Soc.*, 30, 1737.

DISCUSSION.

After the reading of the Papers the subject was thrown open for general discussion.

Dr. H. Borns : Perhaps none of the theories which have been discussed have made many converts. The exhibitors of these fine specimens before us have at any rate solved one side of the problem, that of keeping iron or certain of its alloys passive—how, they will not tell us. But we might try these products in researches. Dr. Senter said it was peculiar that a scratched passive metal should turn active. Why not? Would not strong local action be set up, and might that not account for some other phenomena as well? for the surface of an electrode is never uniform. Might I also ask Dr. Grube how his statement is to be understood, that Le Blanc on the one hand, and Foerster and his pupils on the other, had found that the kathodic deposition of the metals of the iron group takes place at a diminished rate. Dr. Reichinstein's absence is to be regretted also for the reason that he might have explained some of his deductions, which were very difficult to follow; by what kind of mechanism, *e.g.*, is the oxygen to push the metal atoms out of the electrode-volume? As regards Flade, who has been referred to by several authors, I do not quite see why he disregards the third of his possible hypotheses: (1) pure iron is active and is made passive by oxygen (oxygen hypothesis); (2) pure iron is passive and is rendered active by hydrogen (hydrogen hypothesis); (3) the possibility—that oxygen is responsible for the passive, and hydrogen for the active state, and that we have in neither case to deal with natural iron—he does not consider. It might be worth consideration. We know that "pure iron" is anything but pure, and that, when no more gas can be driven out of many metals by heat, kathode bombardment will yield more gas for weeks. Several of the theories reviewed further depend upon electrotonic conductivity of metals. It is perhaps not superfluous to remind members that H. A. Lorentz, of Leyden, in the recent discussion on radiation at the Birmingham Meeting of the British Association, remarked that the electronic theory could no longer be regarded as sufficient. Finally I might mention an experiment recently described by Isgarischew, of Moscow. It concerns solutions in alcohol, not in water; only nickel and copper turned passive in alcoholic solutions of their chlorides, but they did not when all oxygen was excluded and hydrogen passed through the solution. The phenomena, I am inclined to agree with Dr. Senter, are far too complex and varied to fit one universal theory, and I also think that we should heed G. C. Schmidt's conclusion: gases play an important part as catalyst, hydrogen apparently in the first instance; but we know too little about the absorption of other gases by metals.

Dr. E. K. Rideal : As a result of systematic investigation into the electrochemical properties of the elements of the sixth group of the Newlands-Mendeléeff classification which is being carried on at the Technical High School at Aachen the following "passivity phenomena" were observed by Dr. A. Fisher, Dr. A. Roderburg, and myself in the examination of tungsten and uranium.

In the case of tungsten it was found that small quantities of impurities affected the passivity potentials. A metal containing less than 0·04 per cent. impurity was finally obtained; this was superficially fused in vacuo by the Wehnelt-Roderburg apparatus and the surface polished with fine French chalk. It was noted that the nature of the surface had a great influence on

the potentials obtained. Measurements of potential differences between metal and solution were taken with the hydrogen electrode as zero.

The metal was most passive in 4 N. CrO_3, H_2SO_4, giving

$$E_A = + 1{\cdot}013 \text{ volts,}$$

and most active in N. NaOH, giving

$$E_A = - 0{\cdot}676 \text{ volts.}$$

Muthmann and Frauenberger, who used a metal containing a considerable amount of impurity, obtained

$$E_A = + 0{\cdot}883 \text{ volts,}$$

$$E_A = - 0{\cdot}617 \text{ volts,}$$

as maximum and minimum respectively.

In the case of uranium the purest metal that could be obtained still contained 0·40 per cent. impurity; it was submitted to a similar treatment of fusion in vacuo and polishing.

The following potential differences were observed between metal and solutions:

4 N. CrO_3, H_2SO_4, E_A + 1·452 volts;	N. KCl, E_A + 0·150 volts.
	4 N. NaOH, E_A − 0·536 volts.
2 N. CrO_3, H_2SO_4, E_A + 1·015 volts;	2 N. NaOH, E_A − 0·068 volts.
1 N. CrO_3, H_2SO_4, E_A + 0·985 volts;	N. NaOH, E_A − 0·038 volts.

Muthmann and Frauenberger, using a very impure metal, obtained in 4 N. KCl, E_A + 0·190 volts, but they could not cause the metal to become more active.

The general conclusions are:

In NaOH and KCl these metals, if originally passive, become increasingly active on increase of the time of immersion until the stationary value is obtained.

In chromic acid, if the metals are passive to begin with, they increase in passivity until a maximum is reached, after which a small activation results.

This is probably due to the decreasing oxygen content of the solution to interaction with the electrode. This results in a relative increase of the hydrion concentration.

I carried out some experiments on the influence of the small traces of dissolved air which are always present in solutions cooled under ordinary conditions. I found that although the equilibrium or stationary value was not much altered the velocity of attainment was considerably affected.

Average Change in Volts per Hour.

Solution.	Cooled in Air.	Cooled in Hydrogen.
4 N. NaOH	0·021	0·144
2 N. NaOH	0·009	0·015

The velocity is considerably retarded by the presence of minute traces of oxygen.

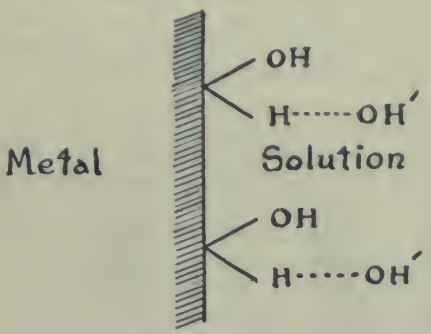
The placing of these elements in the potential series (Spannungsreihe) was difficult owing to—

1. Passivity making the action metal $\rightleftarrows$ ion non-reversible at the critical potential derived from Nernst's equation $E = \frac{RT}{nF} ln \frac{\pi}{P}$. The apparent hysteresis effect exhibited when the potential difference is approached from each side of the equilibrium value vitiates the value of thermo-dynamical treatment unless velocity considerations are taken into account.

2. Hydrolysis of the salts containing W^{VI} and U^{IV}. It was found that the hexachloride of tungsten and the tetrachloride of uranium when dissolved in cold dry ethyl alcohol were comparatively stable; the rate of alcoholysis was measured with indicators and by the conductivity was found to be negligible for a few hours.

Passivity was correspondingly less in alcoholic solution than in aqueous ones. These and many other similar experiments on these metals are in my opinion readily explainable on the following basis:

When the metal is immersed in water the metallic ions at the surface become hydrated, hydration increasing with the valency of the metallic ions. Metals in which this valency is well developed, such as chromium, iron, tungsten, uranium, and tantalum are especially passive; nickel, cobalt, and aluminium are passive in alkaline solutions probably owing to film formation. Decreasing the hydrion concentration in the solution increases the hydroxyl concentration on the surface of the metal; this forms potentially *a hydroxide* (not an oxide as in the oxide theory of passivity).



The hydroxyl groups distribute themselves on the surface uniformly. The reverse effect produces activation.

Ethoxy and methoxy groups do not form methoxides and ethoxides so readily, and passivity is less in consequence.

Mr. H. L. Heathcote: It is now nearly fourteen years since I was first interested in passive iron. At that time the revival of interest had scarcely commenced, and Hittorf's experiments on passive iron had not been published. As those who are familiar with the literature of the subject will know, no one had succeeded in obtaining passive iron in a dry state, there was no consensus as to what constituted a *test* for passivity, the results of different workers were often most contradictory, and the various phenomena were not correlated.

In repeating the conflicting experiments of earlier workers it soon became apparent that an acknowledged standard test for passivity was badly wanted. For this I used dilute nitric acid with a specific gravity of 1·2 at 15° C. This

will not passivify an active piece of iron or steel, although it will co-operate in enabling passivity to spread from a passive part to an active one. This test will therefore not prove that a surface is passive all over; there may be active spots on it. When the piece to be tested is immersed quickly this spreading is less likely to happen. I believe that many apparent contradictions vanish when this test is used to discriminate. It is far less misleading and ambiguous than many that have been proposed, and is particularly appropriate in view of the original meaning of the word "passive."

Another thing that forced itself before my notice was the presence of active spots and crevices on iron and steel passivified in various ways. These go far to account for many of the conflicting results that have been obtained. To get concordant results one has to persevere with each piece of metal until, by polishing and waxing over and etching with nitric acid, it has been got into such a state that the spots that go blue in, say, a 10 per cent. solution of pure potassium ferricyanide in water are very few or non-existent.

Another important step toward producing pure passive iron is made by drying it. The method I used for doing this is published in the *Journal* of the Society of Chemical Industry for 1907, and involves the use of one or two solutions and then washing with absolute alcohol.

As one would expect, passive iron so dried behaves very differently to passive iron covered with an electrolyte. It is not these peculiarities I wish to emphasize, however, so much as the advantages gained by using for one's experiments a pure material. But this is not all. The ferricyanide solutions may enable one to obtain a more uniform raw material, and drying may make it much purer, but unless the pieces are placed in a high vacuum to remove the dissolved or adsorbed gases the raw material has not been purified as far as it can be. Dr. Allen has told us that films of condensed gas cannot be removed from metal surfaces by high vacua. My experiments show, however, that vacua of the order of ·02 mm. mercury can and do remove gases from passive iron.

Passive iron dried according to my directions can be heated in air till too hot to hold without losing its passivity to 1·2 nitric acid, and I submit that workers with passive iron should use these unifying and purifying agencies if they want to study passive iron as such.

On the theoretical side I have very little to say, because from the first my object has been to strengthen resources rather than posit a theory. It does seem certain, however, that the phase which prevents the interaction of 1·2 nitric acid and the active iron underneath must be a solid one. One can press a passive rod with a smooth glass rod until the surface is visibly planished, and even when the glass rod is swiftly removed the planished surface does not become active, as it would surely do if the film were gaseous. Scratching with a broken glass rod activifies the scratched part. This can be shown in an interesting manner by performing the experiment in a 10 per cent. aqueous solution of potassium ferricyanide. In this solution, as also when dry passive iron is used, the surface only becomes active *where it has been scratched.*

Mr. A. T. Smith said that in effect it seemed to him that the passivity of a metal might possibly be dependent on the physical condition of the surface. A rough surface, for example, might and would be probably much less stable than a perfectly smooth or polished surface. In this connection he called attention to a Paper read by Dr. Beilby a year or two back, before the Liverpool Section of the Society of Chemical Industry, in the course of which he exhibited numerous photomicrographs of metallic surfaces in the various stages from a rough to a completely polished one. He showed that an apparently polished surface was in fact deeply furrowed, the edges of the

furrow being sharp. These edges, however, appeared to be, in a sense, fluid, because by continual rubbing with hard and smooth substances they were eventually turned over until, with sufficient care, they might be made to appear almost completely homogeneous, even under high powers of magnification.

He suggested that if a plate of metal were used, the surface of which was perfectly and highly polished, and was then subjected to the delicate tests described by the authors of the Papers, it was quite possible that such a plate would exhibit greater passivity than a similar plate of metal which had not been so highly polished.

Dr. T. M. Lowry was prepared to advocate the oxide-film theory of passivity, if only because it was the only one that he thoroughly understood. It was strange to hear that *aqueous* hydriodic acid contained no oxygen and could not give rise to an oxide film. It was equally unreasonable to suggest that heating in "nitrogen" could not give rise to an oxide film; on the contrary, this appeared to be an excellent method for producing a thin film. The analogy of most other metals would suggest that the oxide was more likely to be in the form of a film than in solid solution in the metal. The instability of the film found an analogy in the readiness with which tinned iron became corroded as soon as the protective layer became damaged and also in the instability of aluminium which had been acted by mercury.

The theory of primary anion discharge was surely a revival of the early theory of Grottlins, and not a modern invention.

Mr. S. A. Main: The scientific aspect of passivity has been very deeply discussed this evening. The practical aspect of this subject, namely, the corrosion of structures of steel, iron, and other metals, is an important one, and has been studied by metallurgists from the earliest times with the view of obtaining non-corrodible materials for various purposes, which are at the same time suitable as regards their mechanical properties. A number of such specimens are exhibited. Sufficient scientific investigation of the nature displayed in the Papers read at this meeting does not seem to have been applied to these alloys, and I would suggest them as materials for research. The results of such investigations would without doubt be of considerable value to metallurgists, and at the same time afford a possible means of discrimination between the various theories of passivity. The properties of more or less pure metals in this connection have been fully discussed, but the alloys, the properties of which have in many cases no resemblance to those of their constituent elements, introduce quite new problems, the elucidation of which might conceivably require modification or alteration of the theories.

Professor Alfred W. Porter, in reply to a question put to him by the Chairman, stated that the validity of Nernst's equation depended upon other factors besides the assumption that the phenomena concerned are reversible. One fundamental assumption is that the pressures concerned follow the laws of gases. As is well known, the logarithmic expression $\log \frac{p_1}{p_2}$ only represents the true expression $\int v dp$ when $pv =$ constant. For dilute solutions this is practically the case. But the approximate expression is also freely used for cases of greater concentration; its use in such cases cannot be justified.

The Chairman, in summing up the Papers and discussion, thanked Dr. Grube on behalf of the Faraday Society for his able contribution to the subject of passivity and for his kindness in coming over from Germany to take part personally in the proceedings of the evening. Thanks were also due to those gentlemen who had exhibited such interesting samples of resis-

tant alloys. He was very sorry that Sir Robert Hadfield, who ought to have occupied the chair that evening, was unable to be present to describe his interesting series of chromium and nickel-chromium iron alloys. He desired, however, to express on behalf of the Faraday Society their best thanks to Sir Robert Hadfield's representative, who had given them such an interesting account of these alloys. The thanks of the Society were also due to Messrs. Lennox for the very interesting and important exhibit of chemical apparatus made of "Tantiron." Coming now to the Papers and discussion on the subject of passivity, he desired in the first place to thank Dr. Senter for his most able and lucid summary of the subject.

With regard to Professor Le Blanc's Paper, it seemed to him (the Chairman) that in explaining the electrode polarization Professor Le Blanc made an unjustifiable use of Nernst's equation. So far as the theoretical deduction and experimental verification of Nernst's equation were concerned, the osmotic pressure (or concentration) of the ions entering into that equation referred to the total ionic concentration. So far as he knew there was no experimental evidence (or theoretical grounds) for assuming that they could apply Nernst's equation to "non-hydrated" metal kations.

With regard to the various modern investigations on passivity phenomena, he was of opinion that they must concentrate their attention on the quantitative measurement of the anodic polarization potential. The correct interpretation of such measurements would in his opinion finally succeed in unravelling the complicated and entangled skein of electrodic actions. Dr. Grube's Paper was a fine example of this method of investigation, as was indeed to be expected of an investigation emanating from the famous Dresden Laboratory, which Professor Foerster had made a *fons et origo* of all that was best in the electrochemical investigation of aqueous solutions.

The fundamental difficulty was the question of interpretation. The view which he (the Chairman) took was this: Nernst's equation was deduced by means of a reversible thermodynamic process. Nevertheless, the result, once arrived at, could in his opinion be applied at every moment to the instantaneous values of the anodic potential at each surface element of the electrode. The case of entropy offered a good example. One could only evaluate the entropy of a given state by means of a reversible thermodynamic process, but, once the expression for the entropy was arrived at, it could be applied to every small volume element of a process which in sum was irreversible.

The difficulty in the present case lay in the correct determination of the instantaneous values of the two variables occurring in the Nernst equation. In his opinion a great deal of the confused notions and opinions concerning the phenomena of passivity were to be ascribed to a failure to appreciate this fundamental point. All the researches and experiments of all the best "practical" men in the world would entirely fail to elucidate the subject of passivity if they did not concentrate their attention on the delicate instantaneous equilibria occurring at each surface element of the electrode. In his opinion Nernst's equation was still the fundamental sheet-anchor of their thought, without which vague drifting was unavoidable.

He would like to ask Dr. Grube, as representing the Dresden Laboratory, what his views on the above question were. The Paper of Dr. Günther Schulze was very welcome, as coming from one who had made such important contributions to the subject of electrolytic valve action. Important as this subject was, it concerned in his (the Chairman's) opinion a "coarser" phenomenon than that of passivity in acid solutions.

Professor Schmidt's experiments and views concerning the catalytic effect of hydrogen in activating metal surfaces were of the greatest interest. The

experimental results formed an important contribution to the subject. But, as Professor Schmidt himself said, further experiments were necessary before his interpretation of the results could be generally accepted. With regard to the Paper of Professor Schoch, he could not see that Professor Schoch's "modification of Nernst's original conception" was one which "follows as a matter of course from our present knowledge of electrons and the immobility of positive electric charges."

The ultimate explanation of electrodic actions would certainly be one in which account would have to be taken of electrons and their mobility. Indeed, this had already been done by many authors. He hoped that Professor Schoch would obtain further and more direct evidence in support of his views.

He (the Chairman) felt he expressed the opinion of the Faraday Society when he said how sorry they were that Dr. Reichinstein was unable to be present to read his Paper. He could not unfortunately enter into a discussion of Dr. Reichinstein's views, as he had not had sufficient time and opportunity to master them.

The interesting experiments of Mr. Stanley Allen on the photo-electric behaviour of active and passive iron showed that passivated iron exhibited a greatly reduced photo-electric activity. Such experiments were somewhat analogous to those which had been made on the metal/air contact potentials of metals. He (the Chairman) had been lately making some experiments on this subject in collaboration with Dr. Thorberger Thorvaldson. The results obtained were quite in harmony with Mr. Allen's view that the surface changes were in close relation to "adsorbed" or "condensed" films of gases, including water vapour.

The experiments which Mr. Spiers had made some years ago were in harmony with this view, as were also the very interesting experiments of the late Mr. John Brown (of Belfast). It was therefore quite possible that passivity phenomena were associated with "condensed" (and perhaps in a certain sense dissolved) gases.

In conclusion the Chairman desired to tender the best thanks of himself and the Faraday Society to all those who had contributed by Papers or otherwise to a very interesting and important discussion.

Dr. J. Newton Friend (*communicated December* 16, 1913): Although numerous theories, put forward by different investigators from time to time to account for the phenomena of passivity, were discussed in the Papers communicated to this Society, no reference was made to the suggestion offered by the present writer, nearly two years ago, that in certain cases the passivity of iron may be due to the presence of traces of the passivifying agent absorbed by the metal.* That iron is slightly porous was proved by immersing Kahlbaum's pure iron foil in concentrated solutions of caustic soda or caustic potash for varying periods of time. After removing and washing thoroughly, the metal was placed in a dish with a small quantity of pure water and gently warmed. When the water had evaporated to very small bulk, traces of sodium or potassium were invariably found on applying the usual flame test. Chemists appeared to be somewhat sceptical as to the correctness of these results, and this scepticism was not reduced when H. B. Baker† failed to confirm the writer's results—a failure that was to be expected, since the conditions were not the same, for not only was Baker's alkali much weaker, but his iron was immersed for a shorter period. Quite recently, however, W. H. Perkins‡ has not only confirmed the writer's

* *Trans. Chem. Soc.*, 1912, 101, 50. † *Ann. Reports Chem. Soc.*, 1911, p. 31.
‡ *Proc. Chem. Soc.*, 1913, 29, 302. Also private communication for which the present writer wishes to thank Mr. Perkins.

results, but has shown them to be true also for barium, lithium, and ammonium hydroxides.

That ordinary steel is porous is a matter of common knowledge to the engineer, who is only too familiar with the "sweating" of hydraulic presses. It is interesting in this connection to note that two years ago Bridgman * found that hardened steel cylinders burst when filled with mercury under pressure considerably more easily than when filled with water or glycerine likewise under pressure. Examination of the fracture showed that the mercury had soaked into the pores of the steel. It was further observed that pressing mercury on to the surface of iron resulted in the penetration of the mercury only when the strain was expansive, in which case the pressure tended to open the pores. A compressive strain such as would be caused by pressing on the outside of a steel ball closed the pores and prevented penetration. Several other examples might be quoted, but these will suffice to show that iron and steel are to be regarded as porous, the extent of the porosity depending upon the physical condition of the particular sample under discussion. We need not be surprised at this, for even such compact material as glass has been proved beyond doubt to exhibit porosity. During the ocean survey made by the officers of the United States Navy it was observed that thick hollow glass balls sunk to great depths in the ocean for an hour or so became more or less filled with water. A careful microscopical examination of the surface failed to reveal any cracks or breakages. The obvious conclusion is that the water had been forced by the enormous ocean pressures (some 5 or 6 tons per square inch) through the pores of the glass.

Granted, then, that iron is to a small extent porous, it is clear that this property may have an important bearing upon the phenomena of passivity, and this aspect of the subject ought not to be ignored. Perkins mentions that in his experiments the iron which had been soaked in alkali and then well washed was liable to pitting when allowed to rust. This is characteristic of the presence of an alkali, where the corrosion of electrolytic iron is concerned, as the writer has already shown.† If, then, such minute traces of alkali are sufficient to cause this pitting, surely these selfsame traces may not be too small to play some part in the phenomena of passivity. The writer does not believe that any one theory of passivity will account for all cases that have been observed. Rather would he suggest that each theory has its value, and that in not a few cases of observed passivity more causes than one are at work.

Dr. G. Senter said that he was in agreement with the Chairman that, although the activating influence of hydrogen was definitely established, the further assumption that pure metals are passive and only become active in the presence of $H^{\cdot}$ ions did not seem to be conclusively proved. Most of the activation results with hydrogen described in the important Paper by Schmidt were not incompatible with the removal of oxygen or a film of oxide from the surface of the passive metal, as the author himself recognized. He (the speaker) thought, however, that, taking everything into account, the oxide or oxygen film explanation of passivity produced in acid media could not be maintained. With reference to Dr. Lowry's arguments in favour of the oxide theory, it should be stated that although it is undoubtedly difficult to free nitrogen completely from oxygen, the nitrogen used in Grave's experiments was carefully purified ; ‡ further, as regards Hittorf's

* *Proc. Amer. Acad. Arts and Sciences*, **46**, 325.
† *Science Progress*, 1913, No. 30, p. 202.
‡ *Loc. cit.*, p. 547.

experiments with aqueous hydriodic acid the point at issue is not the presence of *combined* oxygen, but the question of the liberation of oxygen from the solution under the experimental conditions, and it could be shown that the small amount of oxygen set free at the anode is much too small to produce passivity.* Dr. Lowry had made no reference to some of the strongest arguments against the oxide-film theory, such as the activating influence of rise of temperature.

Dr. G. Grube (*communicated reply*): Dr. Borns has asked me how the following statement in my paper is to be understood: "Le Blanc, on the one hand, and F. Foerster and his pupils, on the other, had found that the cathodic deposition of the metals of the iron group takes place at a diminished rate." The cathodic deposition of a metal from the solution of its salt will then be an instantaneous process when, with cathodic polarization of the metallic cathode immersed in the solution of one of its salts, the metal is deposited as soon as the equilibrium potential, which the electrode assumes in its respective solution, is slightly exceeded. With increasing current density this potential will, when the electrode process is instantaneous, be altered to a very slight degree only, and this change will be in accordance with the change in the concentration of the metallic ions in the immediate proximity of the cathode surface, in the sense of Nernst's formula; thus there will merely be a concentration-polarization. When, however, a greater polarization occurs than would be accounted for by the change in the concentration without our being able to trace this high polarization down to some cause, *e.g.*, the formation of a surface film on the cathode, then we shall have to deal with a cathodic process which is progressing at a restricted rate. In that case we have, in addition to the concentration-polarization, a chemical polarization which is an expression of the small velocity of reaction of that process. The investigations of Le Blanc and of Foerster show that the cathode depositions of the metals of the iron group are such processes of small velocity of reaction.

Professor M. Le Blanc (*communicated reply*, January 14, 1914): In reading the discussion I find little occasion for making any additions to my paper. I shall confine myself to brief comments on some remarks of the other speakers.

Dr. G. Senter says in his introduction, on page 5: (3) "The reaction-velocity theory of Le Blanc. In its most general form this theory states that passivity phenomena are due to slow rate of change (electro-chemical or purely chemical) at the anode. In this form the reaction-velocity theory is little more than a statement of facts. . . ." I cannot agree with this view; the theory did not signify a statement of facts, but signified the introduction of a novel point of view for explaining the facts.

Further, Dr. Senter throughout contrasts in a certain measure the hydrogen activation hypothesis with my theory. I am unable to see in how far there be a contrast. I do not oppose the activation of hydrogen at all; I emphasize myself that catalytic influences are at work. In the paper which I presented to the Deutsche Bunsen Gesellschaft I said (*loc. cit.*, p. 66): "The chemically pure iron described by Kreusler would probably have also been entirely passive anodically." The question of the catalytic activation by hydrogen is merely a special case.

Finally, I recognize, to my great regret, from the remarks made by the Chairman, that my deductions must altogether have been little intelligible to him. Otherwise he could not have reproached me with an "unjustifiable

* Compare Grave, *Jahrbuch der Radioaktivität*, 1911, vol. 8.

use of Nernst's equation, etc." If we make the assumption, as I have done, that the reversible process metal $\rightleftarrows$ free ion is taking place with practically infinite velocity at the anode when the electric current is passing, that the chemical process, ion water $\rightleftarrows$ ion hydrate, is following the former with finite velocity, and that the transition from metal to hydrated ion can only be effected in this way, the potential gradient will merely depend upon the concentration of the free ions, and these ions must therefore be introduced into the equation of Nernst. When the second chemical process should likewise be of infinite velocity, or when we always wait with our measurements till equilibrium has been established, it will be immaterial, of course, for diluted solutions, whether we reckon with the concentration of the free ions or with the concentration of the hydrated ions, or with the total ionic concentration, since these three quantities must be proportional to one another according to the law of mass action and must hence lead to the same values in the measurements of concentration cells. Owing to this circumstance all the ordinary measurements of this kind cannot teach us anything as to the existence of free ions or of hydrated ions.

In my oscillograph experiments, which enable me to determine the variation in the electrode potential during very small periods, I have, in my opinion, to deal with relatively slow chemical reactions, so that the concentration of the free ions may assume other values than those corresponding to equilibrium. Since the equilibrium concentration of the free ions must be considered very small, the fresh formation of a very few metallic ions at the anode, *e.g.*, will already suffice to raise their concentration materially and thus to produce a noticeable polarization which the oscillograph will be able to measure. The total concentration of all the ions will practically remain unchanged meanwhile.

These considerations may perhaps convince the Chairman that his opinions are erroneous.

A PHYSICO-CHEMICAL STUDY OF SODIUM AMALGAMS.

PART II. THE ELECTRICAL CONDUCTIVITY.

By ERNEST VANSTONE.

(*A Paper read before the Faraday Society, Wednesday, November* 26, 1913, Mr. W. R. Bousfield, M.A., K.C., Vice-President, *in the Chair.*)

Previous work has shown that the thermal diagram for sodium amalgams is very complex.* Not only are several compounds shown to exist, but some of these compounds undergo polymorphic changes in the solid state. The investigation of the specific volumes of the solid and liquid alloys added but little to our present knowledge of these substances. It was thought desirable to examine some other physical property which would be likely to show abnormal values when compound formation or polymorphic change occurred.

Guertler has pointed out the great importance of electrical conductivity measurements for determining the constitution of alloys.† Such measurements have already been made for liquid sodium amalgams by Bornemann and Müller.‡ Evidence was obtained of the existence in the liquid state of one compound only, viz., $NaHg_2$.

No reliable measurements of the electrical conductivity of the solid sodium amalgams have been made.

The resistances of a few alloys were determined by Grimaldi,§ but the number examined was totally inadequate for drawing any conclusions as to the constitution of the alloys.

The present Paper deals with the determination of the electrical conductivities of about twenty alloys at room temperature. The composition of the amalgams varied from pure sodium to 54 atoms per cent. of sodium.

The electrical resistance of sodium is much less than that of mercury, so in order to obtain accurate values a long narrow thread of metal must be obtained.

A capillary glass spiral 1 mm. diameter and a metre in length (when unwound) was used. At the ends of the spiral small bulbs were blown, into which were sealed platinum terminals. A glass tap was sealed to one end of the spiral; the other end terminated in a piece of wide glass tube left open.

Mercury was drawn into the spiral and the stopcock closed. The resistance of the mercury between the platinum terminals was measured. The spiral was then filled with the liquid amalgam, using the arrangement previously described for filling pipettes in determinations of the specific volumes.‖ The liquid amalgam was allowed to cool slowly in the vapour jacket. It

* *Trans. Faraday Soc.*, vii., 1911.
† *Zeit. anorg. Chem.*, 1906, 51, 432; *Journal Inst. Metals*, September, 1911.
‡ *Metallurgie*, 7, 1909, 396.
§ *Cim.*, 3, 2311, 1888.
‖ *Loc. cit.*

cooled from the top downwards, and as a result of the contraction on solidification the still liquid alloy in the lower part of the tube was continually drawn up and a uniform continuous thread obtained. The resistance was then measured, the spiral cleaned, and the operations repeated with the same alloy.

It was found extremely difficult to obtain a continuous uniform thread of metal on solidification. In some cases it was found necessary to cool progressively from the bottom of the spiral.

Measurements with the same alloy were repeated until concordant results were obtained.

Measurement of Resistance.—The compensation method, similar to that used by Lees in his work on alloys at low temperature,* and by Guntz in determining the electrical conductivity of the alkaline metals, was employed.† The same current from an accumulator cell E_2 is sent through the alloy and through a standard coil F in series with it. A second circuit contains an

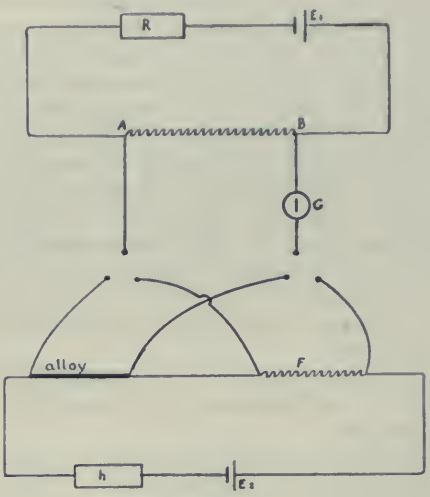


FIG. 1.

accumulator E_1, resistance box R, and a coil of low resistance AB (Fig. 1). The terminals of the alloy, or those of the standard coil, can be connected to the terminals of the coil in the second circuit through a galvanometer and three-way keys P and Q. The difference of potential between the ends of the alloy is made equal to the potential difference between the terminals A and B of the coil by adjusting R until no current flows through the galvanometer.

The potential difference between the terminals of the standard coil F is then made equal to that between A and B by again adjusting R until the galvanometer shows no deflection. The resistance of the alloy is then given by—

$$\left(\frac{R_1 + AB}{R_2 + AB}\right) \cdot F,$$

* *Phil. Trans.*, 1908, 208 A, 427.
† *Journ. chim. phys.*, 7, 1909, 464.

in which—

R_1 = resistance when alloy is compared,
R_2 = resistance when standard coil F is compared.

It was found that a coil of resistance 1 ohm was suitable for F and 5 ohms for AB, so that—

$$\text{Resistance of alloy} = \frac{R_1 + 5}{R_2 + 5}.$$

The alloy was kept at room temperature and readings taken as quickly as possible to prevent error due to alteration in strength of current.

Electrical Conductivity of Sodium.—The sodium used was obtained from Kahlbaum. It was melted under vaseline, drawn up into a pipette, and delivered under vaseline into the tube which was to contain the spiral. The melting-point of the sodium was constant at 97·6° C. The pure sodium prepared by Hackspill *in vacuo* had a melting-point 97·8° C.

The results of the resistance measurements are given below:

Temperature.	Resistance.	Conductivity.	Specific Conductivity.
12° C.	·05173 ·05164 ·05112 ·05131	19·436	$18{\cdot}15 \times 10^{-4}$
	Mean ·05145		

The resistance of the mercury in spiral was ·993 ohm; the specific resistance has been calculated from the following:

$$\frac{\text{Spec. res. of amalgam}}{\text{Spec. res. of Hg}} = \frac{\text{Res. of Na in spiral}}{\text{Res. of Hg in spiral}'}$$

the value for the specific resistance of mercury being known.

The values for the specific conductivity of sodium obtained by other investigators are given below:

Bernini, $18{\cdot}70 \times 10^{-4}$ at 12° C.*
Matthiessen, $20{\cdot}70 \times 10^{-4}$ at 12° C.†
Lohr, $21{\cdot}4 \times 10^{-4}$ at 18·7° C.‡
Guntz and Broniewski, $20{\cdot}99 \times 10^{-4}$ at 12° C.§
Hackspill, $20{\cdot}4 \times 10^{-4}$ at 18° C.‖

The differences in the above values are probably due to impurities in the metal used. Small quantities of other metals lower the conductivity considerably. It will be seen later that 10 atoms per cent. of mercury reduce the conductivity of sodium to half its value. The value for the specific conductivity now obtained agrees best with that of Bernini, who also used sodium not distilled *in vacuo*.

* *Phys. Zs.*, 5, 241, 406, 1904; 6, 958, 1905.
† *Phil. Mag.*, 4, 12, 199, 1856; 13, 81, 1857.
‡ *Wiener Ber. nat. Kl.*, 113, 911, 1904.
§ *Journ. chim. phys.*, 7, 1909, 464.
‖ *Comptes Rendus*, 151, 1910, 305.

The results of the measurements for alloys are given in the following table :

Atoms per Cent. Sodium.	Resistance.	Conductivity.	Specific Conductivity. $\times 10^{-4}$.
96·43	·0695, ·0692, ·0699 ; mean, ·0695	14·37	13·43
94·63	·0802, ·0822 ; mean, ·0812	12·31	11·50
91·33	·0763	13·10*	9·48
87·40	·1165, ·1152 ; mean, ·1158	8·63	8·06
85·43	·1341, ·1224 ; mean, ·1282	7·81	7·29
83·94	·1576, ·1551, ·1635 ; mean, ·1587	6·30	5·88
81·45	·2044, ·1915, ·1968 ; mean, ·1975	5·06	4·73
79·15	·2271, ·2225, ·2215 ; mean, ·2237	4·47	4·17
77·21	·2778	3·60	3·36
75·55	·3800, ·3787 ; mean, ·3793	2·63	2·46
71·78	·5865, ·5812 ; mean, ·5838	1·71	1·60
69·82	·6074, ·6060 ; mean, ·6067	1·648	1·54
67·08	·6419, ·6425 ; mean, ·6422	1·557	1·454
65·52	·6425	1·556	1·453
62·67	·4956, ·5005 ; mean, ·4980	1·556	1·453*
59·86	·4757, ·4753 ; mean, ·4755	1·629	1·522*
58·28	·4159	1·863	1·740*
56·06	·5288	1·891	1·765
55·51	·3872	2·001	1·868*
54·47	·3844, ·3871 ; mean, ·3857	2·008	1·875*

Discussion of Results.—The figures given above show that in the greater number of cases the results agree to within 1 per cent. In some cases, however, with alloys containing a high percentage of sodium, the error is greater, being always in the same direction, giving too large a value for the resistance. This is always due to the extreme difficulty of obtaining a uniform thread of amalgam. The agreement is much better as we pass from the soft alloys to those that are richer in mercury, which are much denser and harder, and have higher melting-points.

It has not been found possible to obtain results for alloys containing more than 45 atoms per cent. of mercury, owing to the continual breakage of the glass spirals.

The results marked with an asterisk were obtained with a second spiral, which was compared with the first by filling with mercury and finding the resistance.

In the diagram (Fig. 2) the specific conductivities have been plotted as ordinates against concentrations as abscissæ. The rapid fall in conductivity from pure sodium to alloys containing 15 atoms per cent. of mercury is observed. The discontinuity at this concentration corresponds with the eutectic point on the thermal diagram.

With alloys having a concentration greater than 15 per cent. mercury, the fall of conductivity is less abrupt. A second discontinuity occurs at a concentration of 22·1 per cent. mercury ; the corresponding break on the thermal diagram occurs at 27 per cent. mercury.

The remaining portion of the diagram shows a very flat minimum at 35 per cent. mercury ; the conductivity then rises very slowly until the limit of the alloys so far examined is reached.

The results already recorded all refer to room temperature, and form the

preliminary work of a more extensive investigation. Experiments have been made to determine the resistances of the amalgams in the liquid and solid states at different temperatures. These are being continued, and determinations of the temperature coefficients carried out.

The expenses in connection with the work have been defrayed by a sum from the Government Grant Committee of the Royal Society, to whom I wish to express my thanks.

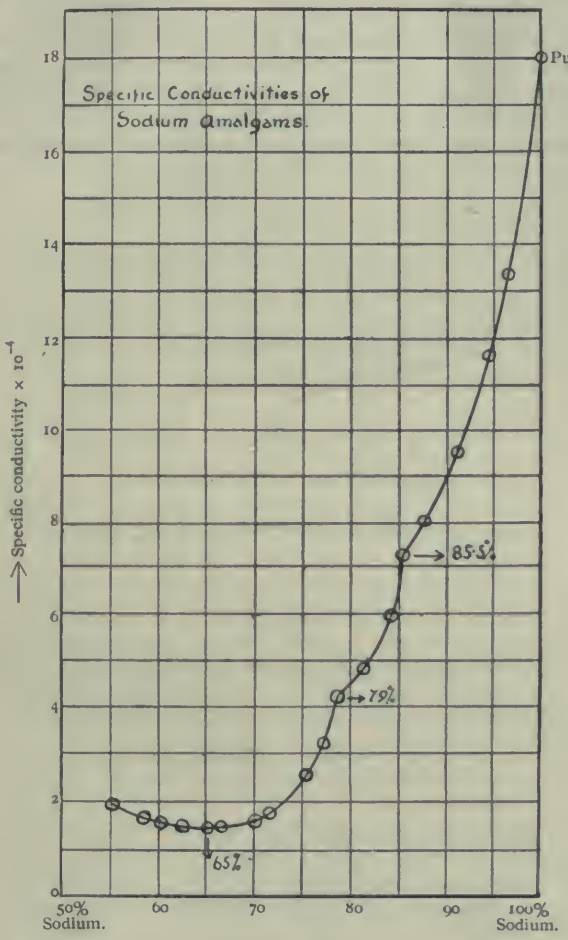


FIG. 2.

The greater portion of the work was carried out at University College, University of London, W.C., and my best thanks are due to Sir William Ramsay and Professor A. W. Porter, F.R.S., for the interest taken in the work and the facilities afforded me.

THE CHEMICAL LABORATORY, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM.

DISCUSSION.

Dr. H. Borns : I am sorry Mr. Vanstone is not present. But Professor Porter, whose name Mr. Vanstone mentions, might be able to answer a question. Vanstone melts his sodium under vaseline, whilst most of the other workers prepared it *in vacuo*. There would probably be less danger of oxidation with the former method ; yet there might be oxidation, and if the experiments were repeated with the same specimen of metal, an accumulative oxidation effect might be noticed. Has that been tried ?

Mr. E. Vanstone (*communicated reply*) : Only a few determinations were made with the same specimen of metal and concordant values for the conductivity were obtained, so that the accumulative oxidation effect suggested by Dr. Borns was not observed. The breaking-up of the metal into globules prevented many determinations being carried out with the same specimen.

THE INFLUENCE OF A SECOND SOLUTE ON THE SOLUBILITY OF ORTHO-PHTHALIC ACID.

By A. C. D. RIVETT, M.A., D.Sc., and E. I. ROSENBLUM, M.Sc.

(*A Paper read before the Faraday Society, Wednesday, November* 26, 1913, Mr. W. R. Bousfield, K.C., Vice-President, *in the Chair.*)

That the solubility of a substance in water may be greatly affected by the presence of a second solute (particularly a salt), even when between the two there is no obvious possibility of chemical action, is a commonplace of laboratory and technical practice. It is perhaps difficult in specific cases to state that no chemical action whatever is occurring between two solutes, but numerous cases are on record in which the actual relations of apparent solubility are in the opposite direction from those which one might expect from any likely chemical reaction.

Extensive measurements have been made by various observers on the alterations of solubility brought about by both salts and non-electrolytes, in substances liquid, solid and gaseous when in contact with their solutions.* For the most part measurements with liquid solutes are of small value, since for adequate theoretical treatment the statement of experimental fact should include analyses of both layers (mainly solvent and mainly solute respectively) as they exist in saturation equilibrium. Such complete analyses have seldom been made, and the failure to carry them out has reduced the value of several considerable investigations such as those of Rothmund and Wilsmore † on the solubility of phenol in water, and of Euler ‡ on that of ethyl acetate. On the basis of his results, which showed a decrease of solubility of the ester in presence of salts (with the effectiveness of the salts in roughly the same order as they appeared in experiments on gas solubilities), Euler concludes that the action of the salt is probably due rather to the ions than to the undissociated molecules.

Measurements on solids have been made by a number of observers, but little attempt has been made to obtain a quantitative expression for the salt influences exerted, though such is needed before the mode of action of the salt may be understood. The application of the theory of an altered internal pressure in the solution § consequent on the presence of the salt does not give results consistent with experiment,|| while a simple hydrate theory attributing alterations in solubility to removal of solvent to form solvates gives inconsistent conclusions when applied to different systems.

* For a very full survey of the literature on this subject up to 1911, see J. Vargas Eyre, British Association Reports, "A Report on Solubility," Part I, 447 (1910) and Part II, 820 (1912). Also, up to 1906, Rothmund, *Löslichkeit und Löslichkeitsbeeinflussung* (Barth, Leipzig, 1907).

† Rothmund and Wilsmore, *Zeitschr. phys. Chem.*, **40**, 611 (1902).

‡ Euler, ibid., **31**, 360 (1899).

§ Tammann, *Ueber die Beziehungen zwischen inneren Kräften und Eigenschaften der Lösungen*, 1907 ; Geffcken, *Zeitschr. phys. Chem.*, **49**, 257 (1904).

|| Levin, ibid., **55**, 527 (1906).

In a paper on the ionic solubility product of weak acids, Kendall* gives figures for the effect of acids of various ionic strengths on the solubilities of a number of weak organic acids. He comes to the conclusion that alterations effected by other acids in the solubilities of these are of two kinds: (1) A decrease in the dissociated portion consequent on the increased hydrogen ion concentration, together with (2) a decrease or increase of the undissociated portion according as this is more or less soluble in the added acid than in water. Such a possible variation in the so-called "constant undissociated value" was first maintained by Arrhenius.† (1) is governed by the law of mass action where weak acids only are concerned; while (2) is specific for any two solutes. If the second of these be a salt it is obvious that the effect corresponding to (1) will be an increase in apparent solubility owing to double decomposition, while (2) will be what is commonly called neutral salt action, and it should be possible to express it in terms of the concentrations of the ionic and unionized fractions of the salt. The constants in such an expression should be a quantitative measure of these salt actions for ions and molecules respectively. The difficulty is to get rid of the effect (1).

In order to obtain more extensive results than have been hitherto available on the solubility of a single substance in various aqueous solutions, and if possible to find some way of expressing the relative effects of salts and other solutes, measurements have been made on the solubility of ortho-phthalic acid in presence of several concentrations of each of some 26 solutes. A non-dissociated substance would have been preferable, but it is difficult to find a slightly soluble one which can be readily estimated with the necessary accuracy. In saturated solutions, the second dissociation of o-phthalic acid will be slight, and it may be regarded as a weak monobasic acid. For comparison of positive radicles the chlorides of Li, Na, K, Rb, Cs, NH_4, H, Mg, Ca and Ba have been investigated, and for negative radicles the four halides, three halates, nitrate and sulphate of potassium. In addition there have been included the nitrate and sulphate of sodium, and also acetic acid, mercuric cyanide, ethyl alcohol, and cane sugar (pure and partly inverted). Measurements have been made at $25° \pm 0·01$; with KCl and $NaNO_3$ at $35° \pm 0·02$ also.

Experimental.

As it is by no means easy to decide the most suitable method of representing concentration, densities have been determined for all solutions, so that the figures quoted on the basis of gram-mols per litre are available on any other basis of representation. Molar concentrations are used, unless otherwise stated, as they are more reasonable than equivalent concentrations when non-electrical properties in other than very dilute solution are concerned.

The method of obtaining saturation with phthalic acid was to shake an excess of twice crystallized acid with the solution under consideration in sealed glass tubes which had previously been steamed for from eight to ten hours. The tubes, eight to each salt, including, usually, one with pure water as a check, were shaken overnight in a modified Noyes apparatus, saturation being always attained in considerably less than this time. In some cases the solutions were heated before immersal in the bath, saturation being attained more rapidly from the side of supersaturation. Samples of about 30 c.c.

* Kendall, *Proc. Roy. Soc.*, A, **85**, 200 (1911).
† Arrhenius, *Zeitschr. phys. Chem.*, **31**, 197 (1899).

were removed by a pipette carrying a cotton-wool filter, and duplicate titrations, against standard solutions of baryta with phenolphthalein as indicator, were made on each tube. These were carried out by weight: the bulk of the acid was neutralized by 0·1-equivalent normal baryta, and the end point determined with 0·02-normal. The differences between duplicate titrations of the same tube were seldom as great as 1 in 500. But completely different sets of measurements of the solubility in pure water showed differences as high as 1 in 200, which may be regarded as the possible experimental error of the work. Densities, determined with pyknometer or pipette, are correct to 1 in 5,000.

With potassium fluoride all tubes, pipettes, and beakers were coated internally with paraffin wax. With ammonium chloride difficulties in the way of titration made it necessary to adopt another method, namely, that of determining gravimetrically on a Gooch filter the phthalic acid remaining undissolved after shaking a known amount of solution with a known excess of acid. For the acids, hydrochloric and acetic, still another method was used, the estimation of a very small amount of phthalic acid in presence of a large excess of another acid not being accurate by titration. The form of tube used is shown in Fig. 1.

FIG. 1.

A rubber cap A fits on a narrow tube widened to a bulb B about $\frac{1}{8}$ inch in diameter. This bulb is crossed at its greatest diameter by a perforated platinum plate sealed all round its edge to the glass. A thick asbestos pad *b* almost fills the lower part of the bulb. C is the ordinary steamed tube, and is continued into a narrow tube carrying a tap D (lubricated with a mixture of rubber, paraffin wax, and oil) and turned upwards at the end. E is a rubber cap.

Solid phthalic acid is placed in C, slightly moist, before the filter tube B is sealed in position. The whole tube is then dried by immersion in a wide tube in a bath at 85°, while a current of dried air is drawn through it. When dry and cool it is weighed, and the solution to be examined is drawn in through D by suction at B. When sufficient has entered, the tap D is turned off and liquid in the tube beyond D removed with filter paper. The full tube is weighed and the weight of solution obtained. Caps A and E being fastened in position, the tube is shaken in the thermostat as long as necessary. The saturated solution is then drawn off (while the tube is still in the bath) through the filter *b*, the tube being drained as thoroughly as possible. It is then dried and weighed, and the difference between the first and last weighings gives the weight of acid dissolved. The method is fairly rapid, and though more accurate than a long evaporation of filtered solution, it is less so than the method used for the salts, and the worst error in reproducing results is 1 in 80.

Either Merck's guaranteed or Schuchardt's puriss. salts, twice or thrice crystallized, were used. The phthalic acid was Merck's, and was twice crystallized.

Table I contains a summary of the experimental results. The solubilities of phthalic acid are given in terms of the value in pure water determined in the same set or the preceding one. The value for this in gm.-mol per litre is 0·04185, this value being the mean of the following separate determinations, each the mean of two titrations (the figures are multiplied by 10^4): 419, 418, 418, 418, 418, 418, 420, 417, 420, 419, 418, 418, 418, 418. Density of saturated solution is 1·0022.

TABLE I.

Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
LiCl ...	0·0827	1·0043	0·985	0·984	− 0·1
	·1957	1·0072	·950	·944	− 0·6
	·3322	1·0104	·902	·898	− 0·4
	·5354	1·0152	·827	·831	+ 0·5
	·815	1·0217	·737	·745	+ 1·1
	1·250	1·0320	·616	·618	+ 0·3
	1·727	1·0430	·497	·490	− 1·4
NaCl ...	0·1271	1·0072	0·982	0·985	+ 0·3
	·2439	1·0119	·952	·952	0·0
	·4934	1·0219	·880	·883	+ 0·3
	·9697	1·0404	·751	·752	+ 0·2
	1·601	1·0652	·591	·586	− 0·8
	2·203	1·0868	·476	—	—
	2·978	1·1131	·363	—	—
KCl ...	0·0957	1·0067	1·013	1·0165	+ 0·35
	·2571	1·0139	·995	0·998	+ 0·3
	·5549	1·0279	·954	·954	0·0
	·8635	1·0415	·904	·905	+ 0·1
	1·299	1·0606	·830	·831	+ 0·1
	1·808	1·0823	·744	·744	0·0
	2·690	1·1195	·610	—	—
RbCl ...	0·0779	1·0088	1·016		
	·2459	1·0232	1·023		
	·4558	1·0420	1·009		
	·772	1·0695	0·978		
	1·142	1·1009	·937		
	1·598	1·1370	·883		
	2·085	1·1810	·821		
CsCl ...	0·0692	1·0106	1·026		
	·1961	1·0270	1·043		
	·3444	1·0459	1·052		
	·5653	1·0742	1·058		
	·804	1·1043	1·058		
	1·144	1·1473	1·050		
	1·476	1·1881	1·032		
NH_4Cl ...	0·0587	1·003	—		
	·1403	1·005	0·99		
	·286	1·007	·96		
	·580	1·012	·92		
	·888	1·016	·885		
	1·350	1·023	·82		
	1·895	1·031	·735		
$MgCl_2$ ...	0·0628	1·0073	0·988	0·986	− 0·3
	·1236	1·0117	·951	·945	− 0·7
	·2690	1·0229	·855	·855	0·0
	·4212	1·0344	·765	·767	+ 0·3
	·655	1·0532	·635	·636	+ 0·2
	·9215	1·0712	·507	(·498)	(− 2·0)
	1·317	1·0988	·365	—	—

Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
$CaCl_2$ ...	0·0442	1·0065	1·005	1·001	−0·4
	·0877	1·0103	0·974	0·975	+0·1
	·2945	1·0287	·861	·857	−0·5
	·4576	1·0417	·768	·772	+0·7
	·6716	1·0608	·667	·659	−1·0
	·861	1·0766	·584	·585	+0·2
	·948	1·0843	·546	·547	+0·2
	1·461	1·1262	·374	—	—
	3·038	1·2500	·117	—	—
	4·299	1·3433	·0673	—	—
$BaCl_2$ ...	0·0488	1·0110	0·997	0·999	+0·3
	·0956	1·0160	·971	·974	+0·3
	·1770	1·0359	·934	·933	−0·1
	·3103	1·0590	·877	·872	−0·6
	·4615	1·0854	·811	·810	−0·1
	·676	1·1250	·714	·729	(+2·1)
HCl ...	0·217	1·006	0·768	0·766	−0·3
	·639	1·013	·697	·698	+0·2
	1·175	1·020	·620	·613	−1·2
	1·915	1·034	·494	·494	0·0
	1·936	1·035	·486	·490	+1·0
KBr ...	0·0846	1·0095	1·013	(1·021)	(+0·8)
	·1760	1·0170	1·010	1·015	+0·5
	·3295	1·0300	0·996	1·000	+0·4
	·5586	1·0486	·971	0·973	+0·2
	·808	1·0693	·938	·944	+0·6
	1·828	1·1523	·785	·782	−0·3
KI	0·0963	1·0139	1·014	—	—
	·1893	1·0248	1·029	1·034	+0·5
	·3623	1·0451	1·021	1·023	+0·2
	·6713	1·0823	1·000	0·998	−0·2
	1·250	1·1502	0·947	·941	−0·7
	1·510	1·1800	·913	·912	−0·1
	1·981	1·2333	·851	·849	−0·2
$NaNO_3$ ...	0·2518	1·0132	1·004	1·006	+0·2
	·487	1·0242	0·981	0·981	0·0
	·998	1·0469	·923	·922	−0·1
	1·488	1·0678	·861	·861	0·0
	1·962	1·0885	·795	·799	+0·6
	2·463	1·1097	·731	·729	−0·3
	2·981	1·1308	·667	·658	−1·4
$Hg(CN)_2$ ...	0·0304	1·008	1·003	1·005	+0·2
	·0668	1·016	1·011	1·011	0·0
	·1733	1·036	1·030	1·030	0·0
	·2959	1·060	1·050	1·050	0·0
	·4000	1·080	1·069	1·068	−0·1
C_2H_5OH ...	0·1015	1·0019	1·014	1·015	+0·1
(Schuch.	·1930	1·0008	1·027	1·028	+0·1
99½ per cent.)	·3723	0·9994	1·058	1·054	−0·4
	·646	·9970	1·097	1·094	−0·3
	·946	·9934	1·143	1·137	−0·5
	1·433	·9814	1·235	—	—
	2·026	·9829	1·366	—	—

Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
Cane sugar	0·1547	1·0230	0·974	0·976	+ 0·2
	·2962	1·0413	·955	·956	+ 0·1
	·6199	1·0637	·909	·907	— 0·2
	·950	1·1245	·864	·857	— 0·7
	1·426	1·1860	·822	·786	(— 4·5)
Cane sugar partly inverted.	0·0804	1·014	0·983		
	·1930	1·029	·957		
	·399	1·056	·914		
	·620	1·086	·862		
	1·255	1·172	·709		
	1·950	1·253	·578		
KF	0·1147	1·0108	2·448		
	·2925	1·0245	4·434		
	·5746*	1·0412	6·410		
$K(C_2H_3O_2)$	0·0893	1·0110	3·040		
	·1984	1·0216	5·536		
	·3291	1·0280	7·04		
	·3384	1·0352	8·64		
	·547*	1·0453	11·9		
KNO_3 ...	0·1058	1·0085	1·029		
	·1935	1·0140	1·042		
	·3353	1·0243	1·056		
	·5447	1·0355	1·058		
	·902	1·0567	1·056		
	1·100	1·0682	1·052		
	1·269	1·0788	1·042		
	1·622	1·0995	1·019		
	2·196	1·1321	0·977		
K_2SO_4 ...	0·0265	1·0056	1·073		
	·0424	1·0079	1·102		
	·1063	1·0167	1·173		
	·2104	1·0310	1·231		
	·3721	1·0552	1·282		
	·6271	1·0854	1·312		
$KClO_3$ ...	0·0282	1·0034	1·013		
	·1051	1·0095	1·023		
	·2085	1·0180	1·030		
	·3041	1·0252	1·029		
	·4055	1·0327	1·028		
	·5109	1·0406	1·026		
	·6126	1·0483	1·016		
$KBrO_3$ ...	0·0192	1·0040	1·014		
	·0611	1·0099	1·023		
	·1312	1·0180	1·029		
	·2306	1·0300	1·033		
	·3902	1·0398	1·030		
	·4300	1·0432	1·027		

* At the next higher concentration, potassium hydrogen phthalate separated.

Salt.	Salt Conc. Molar.	Density.	Relative Solubility (Expt.).	Relative Solubility (Calc.).	Percentage Error.
KIO_3 ...	0·0147	1·0043	1·011		
	·0317	1·0077	1·023		
	·0924	1·0186	1·061		
	·1525	1·0294	1·089		
	·2314	1·0433	1·125		
	·2901	1·0537	1·145		
	·3716	1·0678	1·176		
Na_2SO_4 ...	0·0541	1·0088	1·048		
	·1428	1·0200	1·088		
	·567	1·0704	1·072		
	·898	1·1082	0·952		
	1·205	1·1418	·833		
	1·517	1·1750	·721		
$H(C_2H_3O_2)$...	0·1905	1·003	1·034		
	·3484	1·004	1·063		
	·732	1·008	1·177		
	1·039	1·011	1·245		
	1·523	1·016	1·372		
	2·016	1·020	1·575		

The results are graphically shown in Figs. 2 and 3, where the order of effect of the various solutes is at once obvious. Molar concentration of solute is here plotted against relative solubility of phthalic acid in the solution, and each vertical division is a decrease of 0·1 in the latter. The general form of curve is the customary one of a more or less considerable initial rise followed by a more or less sharp fall.

Since phthalic acid is a weak electrolyte, some double decomposition with the salts is to be expected, and this is evidently represented in this initial rise. In those cases where a maximum (in some it is not very high) is reached and passed the decrease of solubility consequent on the so-called neutral salt effect has overcome the increase caused by double decomposition. The apparent increase will of course be greatest in the cases of salts of acids comparable in ionic strength with phthalic acid. Thus with potassium acetate and fluoride the immediate increase in solubility of the acid is very great, the rise being from 0·0418 to 0·45 molar normal, at which point potassium hydrogen phthalate begins to separate. This rise is too rapid to be shown in the figures.

When the curves are considered in order, it is apparent at once that in general it is the least electro-positive element which exerts the greatest depressing effect among the chlorides, both in the univalent and divalent metals. The curve for ammonium chloride is represented by dots to indicate that the experimental error in its determination is greater than that for the other salts. Among potassium salts, the order of effect among negative radicles is the same, that is to say, the most electro-negative or least electro-positive anion has the greatest depressing effect. Oxy-radicles give maximum points very high.

Comparing the pairs of salts of sodium and potassium in Fig. 3 (III) it is seen in each case that the sodium salt lessens the solubility more than the corresponding salt of potassium. Lundén* found the same thing in his work on ethyl acetate with salts of these two metals.

* Lundén, *Journ. Chem. Soc.*, Abst., **102**, ii. 911 (1912).

To test whether there is a temperature coefficient to the effect of the salt upon the solubility of the acid, as is to be expected where chemical action in the ordinary sense is the main factor, measurements have been made with two salts at 35°, viz., KCl and $NaNO_3$. The results are detailed in Table II, and the relative lowerings at 25° and 35° are plotted in Fig. 4. It is clear that there is a temperature coefficient, but for part of their lengths the curves, especially those for KCl, run almost parallel. This is interesting, as it may

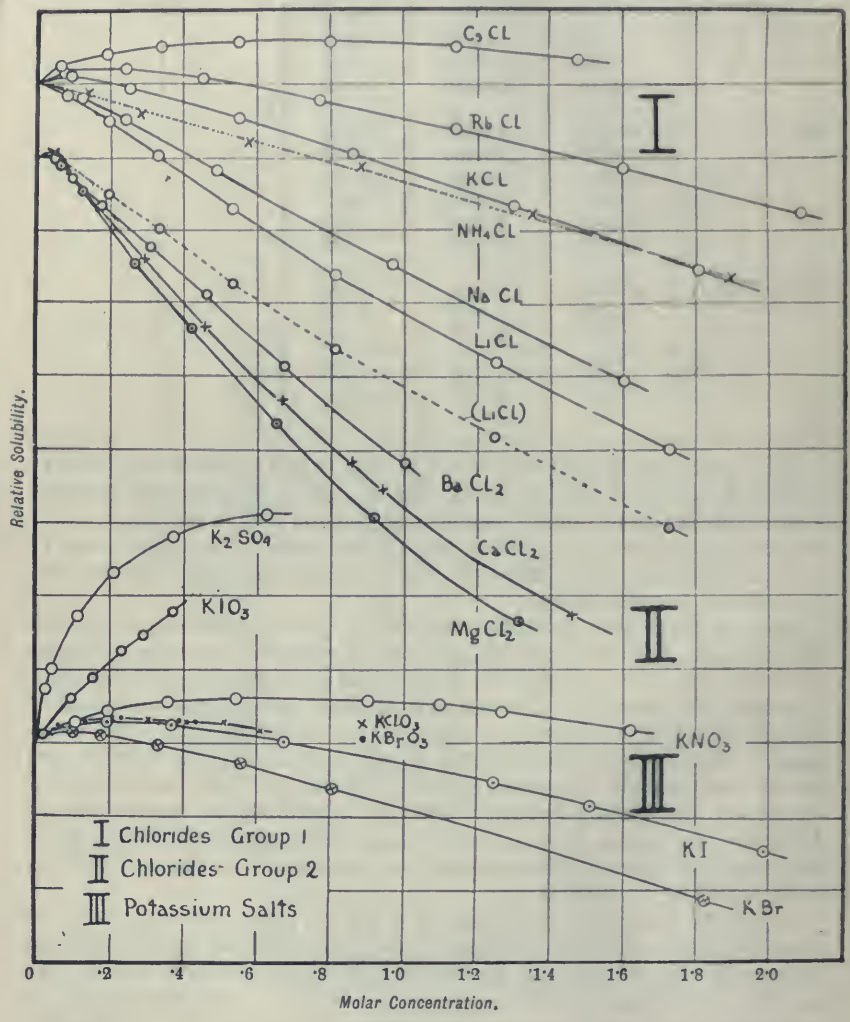


FIG. 2.

be that in these latter portions of the curves a purely physical influence, without any considerable temperature coefficient, is concerned, while at the beginning of the curves the phenomenon is mainly chemical and with a co-efficient. It will be seen that the lowering of solubility (value in pure water at the respective temperature = 1·000) is greater at the higher temperature than at the lower, as Hoffmann and Langbeck* found for other acids.

* Hoffmann and Langbeck, *Zeitschr. Phys. Chem.*, 51, 385 (1905).

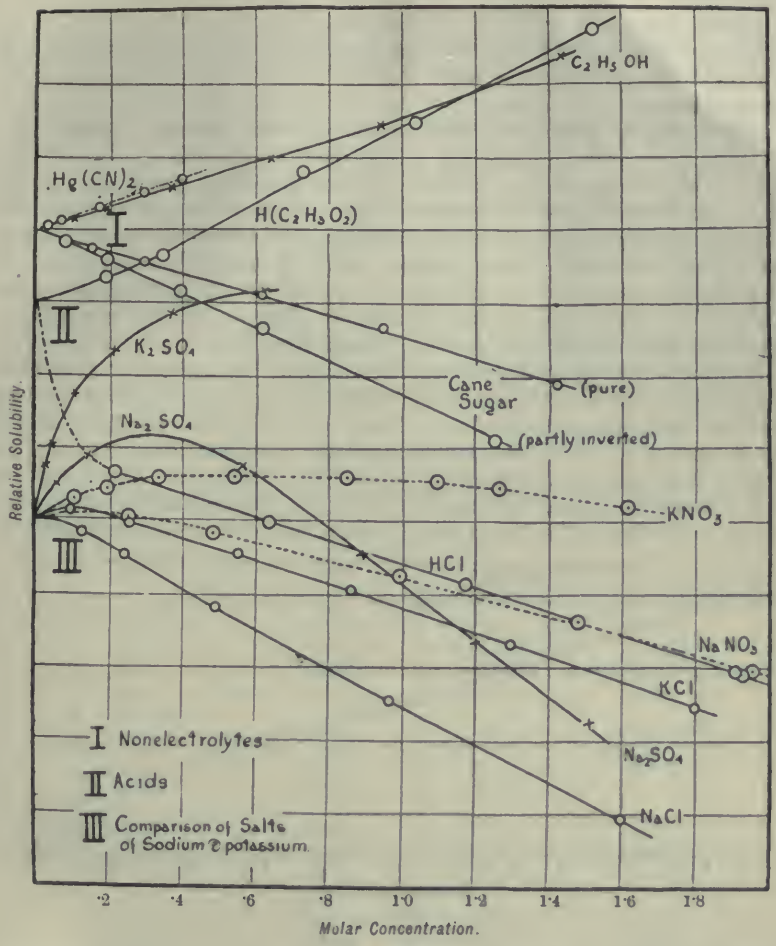


FIG. 3.

TABLE II.

Temperature 35°. *Solubility of Acid in Pure Water* = 0·0610 *norm.*

Salt.	Salt Conc.	Density.	Relative Solubility (Expt.).
KCl	0·0761	1·0063	1·006
	·1603	1·0097	0·989
	·339	1·0180	·972
	·674	1·0328	·917
	1·011	1·0480	·860
	1·541	1·0702	·766
	2·058	1·0925	·678
$NaNO_3$ ...	0·0748	—	1·0024
	·1708	1·0066	0·998
	·396	1·0248	·964
	·745	1·0423	·912
	1·125	1·0629	·848
	1·727	1·0940	·754
	2·294	1·1226	·663

Further Discussion of Results.

In terms of any simple theory of solutions it is not possible to explain fully such results as are here given, but it is worth while to bring forward certain points of interest in the curves.

Any attempt to differentiate between the action of ions and undissociated salt molecules in these solubility phenomena brings one at once to the difficulty of finding a proper expression for the degree of dissociation of the salt. Calculations based on conductivity measurements are to be suspected because nothing certain is known as to the relations between ionic mobility and solution viscosity. Values deduced from freezing-point measurements are probably worse. All that can be done is to admit the possibility of error and take the least objectionable course of using degrees of dissociation calculated from conductivity data in the ordinary way.

A further difficulty in discussing the curves of Figs. 2 and 3 is presented in the initial portion. The rise is doubtless due in part to chemical double decomposition, but since salts do not dissociate in accordance with the simple law of mass action it is not possible to obtain an accurate expression for it. Some of it may be due to increased dissociation of the acid.* But it will be noticed that in a number of cases this initial rise is comparatively slight, the influences tending in the direction of lessened solubility soon exceeding those

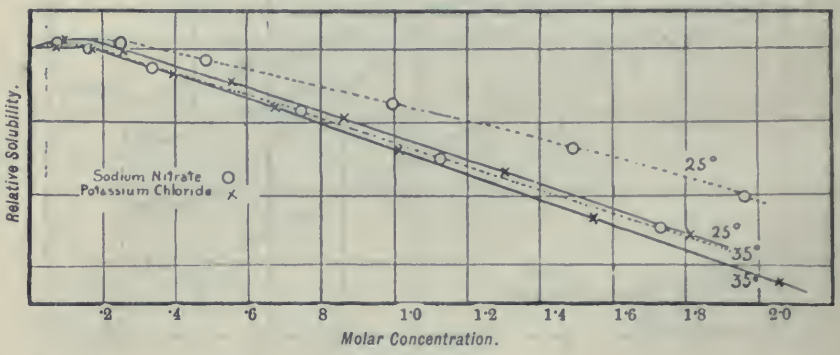


FIG. 4.

giving an increase in apparent solubility. As salt concentration increases, the latter will not increase proportionately and at a sufficiently high concentration it will be slight compared with the decrease due to the so-called neutral salt action. In fact, the form of the latter part of the curve will be determined mainly by the direct action (of whatever kind) of salt ions and molecules on the solubility, but not double decomposition, of the acid. If then this curve be extrapolated to cut the relative solubility axis, a value S_0 will be obtained, representing approximately what the concentration of phthalic acid would be in pure water if those conditions alone ruled in approaching it which determine the latter part of the curve, beyond the initial maximum. Putting S as the calculated solubility we should have—

$$S = S_0 \{1 + k\alpha C + k'(1 - \alpha)C\}$$

where α is the degree of dissociation of the salt at concentration C, calculated from the best figures quoted in Abegg's *Handbuch*. Here it is assumed that the salt action is exerted on all the dissolved acid, not merely on the undissociated fraction: for the testing of a relation between salt concentration

* Bohdan von Syzszkowsky, *Zeitschr. phys. Chem.*, **58**, 420 (1907); **63**, 421 (1908); **73**, 269 (1910).

and undissociated acid, as suggested by Kendall,* more information is required than is available regarding the dissociation of phthalic acid in presence of salts, especially if it is possible that the extent of this dissociation is greatly affected by the salts.

Choosing suitable values for k and k', which we may call the ionic and molecular constants of "neutral salt action" respectively, the values in column 5 of Table I (here expressed in relative figures) are obtained, and in the 6th column are the percentage differences between these and the figures obtained by experiment. It is possible to calculate for those salts only where the initial rise of the curve is slight, but in the list of those examined there are ten available for such calculation, as is hydrogen chloride also. k is calculated as the constant for a single chlorine ion plus its positive partner, that is, concentrations are calculated in equivalents. For convenience equivalents have been used also for k', though where molecules only are concerned, the molar concentration is the more reasonable. The values of S_o, k, and k' are summarized in Table III.

TABLE III.

Ionic and Molecular Constants of "Neutral Salt Action."

Salt.	S_o.	k.	k'.
HCl	0·0330	−0·20	−0·20
LiCl	·0425	−0·41	−0·16
NaCl	·0428	−0·30	−0·21
KCl	·0431	−0·057	−0·415
$\frac{1}{2}MgCl_2$	·0430	−0·395	−0·18
$\frac{1}{2}CaCl_2$	·04325	−0·40	−0·096
$\frac{1}{2}BaCl_2$	·0430	−0·395	−0·00
KCl	·0431	−0·057	−0·415
KBr	·0427	+0·115	−0·85
KI	·0433	+0·102	−0·71
$NaNO_3$	·0430	−0·072	−0·16
$Hg(CN)_2$	·0420	—	+0·085
C_6H_5OH	·0418	—	+0·145
$C_{12}H_{22}O_{11}$	·0420	—	−0·15

Looking at the figures in column 6 of Table I, it is seen that except in the stronger salt solutions, where the calculation of the degree of dissociation is very uncertain by reason of ignorance of the relation between ionic mobility and solution fluidity, the percentage error in the calculated relative solubility as compared with the found fluctuates irregularly, and seldom reaches the limit of error of the determinations. In fact, one is able to express with considerable accuracy the decrease of saturation concentration of phthalic acid in terms of the concentrations of the added ions and molecules.

The constants involved are nearly all negative, and for the three ions of potassium, sodium, and lithium (each with chlorine) k increases, while for the chloride molecules k' decreases arithmetically as positivity decreases. For the second group metals the opposite holds for k', while the ionic constants are practically identical for all three, having a slightly lower value than that of the lithium and chlorine ion pair.

* Kendall, *loc. cit.*

Comparing the three halides of potassium, it is seen that the order of constants is not that of the anion atomic weights, and for the bromide and iodide the ionic constants are positive. This latter fact is rather unexpected, though there would seem to be no reason why positive ionic constants should be considered unlikely. It is not possible to separate the effects of any two oppositely charged ions, but it would seem probable, when one considers the ionic constants for the various chlorides, that the value is strongly negative for the ions of chlorine, lithium, sodium, barium, calcium, and magnesium, and possibly positive for potassium and nitrate ions (and possibly the anions of sulphate and oxyhalides). In the case of hydrochloric acid (Fig. 3, II), for which the ionic and molecular constants of the later part of the curve are equal, there is at the initial portion of the curve a rapid drop due to the common hydrogen ion. But in the case of the other acid examined, acetic, either the small amount of acetate ion present, or, more likely, the acid molecules, exert so strong a positive effect as completely to overwhelm any decrease in solubility due to the common ion. The formation of a soluble compound between the two acids, acetic and phthalic, naturally suggests itself to account for this, but any such formation would probably be due to the oxygen in the molecules, and therefore one would expect to find in aqueous solution a considerable hydration of acetic acid. But judged by freezing-point measurements this does not seem to be the case to any considerable extent, as the lowerings in acetic solutions are not greatly different from those calculated on simple theory. A positive action, possibly not chemical in the ordinary sense, therefore seems likely, and in that case it is not improbable that ions and salt molecules may also have positive effects.

Undissociated solutes can possess but one constant—that is, the curves of relative solubility of phthalic acid should be straight lines. To about 1 in 200 this is the case in solutions of ethyl alcohol and cane-sugar up to 1-normal, the constants being here positive and negative respectively. The case of mercuric cyanide is probably accounted for by double decomposition; it gives a very good straight line with k' positive.

Whatever may be the mechanism of the action which shows itself in the altered solubility in presence of salts, of such a solute as phthalic acid, whether it be hydrate formation and consequent removal of water from its solvent rôle or "secondary" influences not properly regarded as chemical, some connection may be expected between the degree of reduction of solubility and the amounts of the various new constituents present as the result of salt addition. Possibly the number of these (ions and molecules, variously complex and hydrated) is so great that so many constants become necessary as to make the resulting equation worthless when applied to results liable to experimental error. But it is at any rate of interest to see, as may be done to some extent in the present case, how far a relation can be applied which takes account of the two main portions of the dissolved salt.

A comparison of various forms of so-called neutral salt action such as are shown in freezing-point lowerings,* solubility alterations, changes in reaction velocity,† and in rate of diffusion,‡ seems to show that the order of effect of the salts is not such as to justify a supposition that a specific salt property is the common and sole cause in all cases. The sequence of salt effect may be different in these different cases, or even in the same case, such as that of freezing-point lowering, with different second solutes. Any constants, therefore, which connect salt concentration with the modified

* Rivett, *Zeitschr. phys. Chem.*, **80**, 537 (1912).
† *Idem*, ibid., **85**, 113 (1913). ‡ Abegg, ibid., **11**, 248 (1893).

property of a second solute would seem to depend, not only on the nature of the salt, but also on that of the particular second solute (possibly with varying temperature coefficients in either case). Until the latter factors can be allowed for, it does not seem probable that a *prima facie* likely common cause can be quantitatively demonstrated in the various phenomena grouped together loosely as examples of neutral salt action.

UNIVERSITY OF MELBOURNE, AUSTRALIA,
1913.

DISCUSSION.

Dr. T. Martin Lowry referred to the fact that a Paper by Dr. Philip on the "Influence of Electrolytes and Non-Electrolytes on the Solubility of Gases in Water" had been published as a contribution to the General Discussion on "Hydrates in Solution."* The work of Dr. Rivett and Mr. Rosenblum, in which a solid was used instead of a gas, had been admirably carried out, and the multiplication of similar data could not fail to throw light on the difficult problem of the real nature of aqueous solutions.

Dr. E. K. Rideal asked Dr. Rivett what led him to the choice of ortho-phthalic acid as a solute, for we have plenty of chemical evidence that, in the case of this acid, the two carboxyl groups do not function equally in the molecule. This is easily seen in the asymmetry of the acid chloride. If, as we have reason to suppose, the solubility is affected by the degree of hydration of the substance either dissociated as ions or undissociated as molecules, and if the second solute may be regarded as affecting this degree of hydration, it would seem preferable to make use of a substance which would "hydrate" in as simple a manner as possible, and not use o.-phthalic acid, in which substance the hydration in solution is probably very complicated.

The **Chairman** observed that to a person, like himself, specially interested in the hydrate theory, the Paper was useful; but he would like to be able to compare the author's curves with curves obtained by the use of another comparison solute. The idiosyncrasies of the curves were the idiosyncrasies of the various salts, and one would like to see how far they persisted when another comparison solute was used instead of ortho-phthalic acid. Dr. Philip had obtained some comparable results by the use of hydrogen as a comparison solute.† Probably organic radicles resembled hydrogen in having little or no water associated with them in solution.

* *Trans. Farad. Soc.*, 1907, **3**, pp. 123–163.
† *Loc. cit.*, p. 29.

OVERVOLTAGE.*

By Professor J. W. RICHARDS (Lehigh University).

DISCUSSION.

(*Held on Wednesday, November 26, 1913, Mr. W. R. Bousfield, M.A., K.C., Vice-President, in the Chair.*)

Dr. A. J. Allmand (*communicated*) : I fail to see exactly what Professor Richards has proved in his Paper. The experimental results could of course have been predicted with certainty beforehand. With an arrangement such as he employed, in which presumably hydrogen and oxygen were the sole products of electrolysis, no ozone or other oxidizing material being formed and concentration changes being negligible, then with an excess of heat produced irreversibly in the cell, the chemical work done by the current *must* necessarily correspond to the total energy change associated with the combination of hydrogen and oxygen to form liquid water (present as dilute sulphuric acid), and this, as Professor Richards points out, means a consumption of 1·48 to 1·49 volts (heat of reaction per gram-equivalent about 34,180 calories). Energy corresponding to 1·23 volts is absorbed in the reversible decomposition of the solution, and energy corresponding to 0·25 to 0·26 volt taken up directly as heat from the cell. If it were not for the heat produced in the electrolyte and (irreversibly) at the electrodes, the cell mentioned would cool during the electrolysis, and the volts absorbed would be considerably less than his theoretical value of 1·49. Nor do his results shed any light on the question of the nature of overvoltage—as to whether this complex phenomenon is due merely to ohmic resistance, as he suggests, or whether it is associated with the doing of chemical work, followed by the degradation of the chemical energy to heat energy. The balance of evidence at present, more particularly work done in Foerster's laboratory at Dresden, appears to me to favour the second hypothesis.

In any case, the "practical" decomposition voltage, which Le Blanc is presumably referring to in the passage mentioned, should be sharply distinguished from the "reversible" decomposition voltage. And this last value corresponds to the change in free energy, not the change in total energy, as Professor Richards has it.

Mr. U. R. Evans: Three assumptions seem to have been made by Professor Richards and some other recent contributors on this subject, which appear to me unwarranted :—

(1) That overpotential is a unique phenomenon, requiring a special explanation, and finding no analogy in general chemical experience.

(2) That overpotential involves necessarily some irreversible electrodic change.

(3) That overpotential is essentially a wasteful factor, economically to be regretted.

* This Paper was published in the Transactions (vol. ix., parts 1 and 2) issued in July, 1913, *supra* p. 140.

It seems best to view the position in this way. Imagine a bright platinum cathode immersed in normal sulphuric acid, and suppose the p.d. to be depressed (made more cathodic) by the application of an external e.m.f. When the p.d. reaches 0·0 volts it may be supposed that, in a state of equilibrium, the platinum is saturated with hydrogen at atmospheric pressure. If the p.d. is made slightly negative (more cathodic still) the electrode must become supersaturated with hydrogen. The evolution of the gas *in bubbles* does not necessarily commence. If the arrangement is favourable the liberation of hydrogen by *diffusion* through the electrodes may occur, but the formation of bubbles will require a considerable degree of supersaturation, which can only be obtained by making the p.d. appreciably more negative than 0·0 volts. The amount of this excess p.d. (overpotential) varies between $-0{\cdot}01$ volts for black platinum and $-0{\cdot}7$ volts for mercury; it is greater in the case of smooth electrodes than rough, bright platinum showing an overpotential of $-0{\cdot}08$ volts.

Qualitatively a complete analogy is shown in the non-formation of steam-bubbles in water heated above 100° C. If air-free water is heated to 100° C., the vapour pressure becomes equal to 1 atmosphere. When it is heated above that temperature, the vapour pressure exceeds 1 atmosphere, but in general ebullition does not commence. The amount of superheating needed to start bubble-formation varies with the material of the containing vessel, and particularly with the nature of the surface, being greater for smooth than for rough vessels. The analogy between superheating and overpotential is qualitatively complete, and it at once suggests itself that the same explanation would hold in both cases. Superheating is believed to be a surface tension effect, connected with the fact that minute bubbles are—on account of their very great surface energy—very unstable things. The work of Moeller has shown a very close connection between the surface tension of the several measurements (measured against hydrogen) and the overvoltage needed for the production of hydrogen bubbles on these metals. It would appear therefore that the two phenomena are to be explained in a similar way.

The only real objection urged against the surface-tension view of overpotential is that the amount of electrodic supersaturation required to explain overpotential is very large compared to the excess value of the vapour pressure needed for ebullition in a liquid. This, however, will be understood, if a comparison is made between the two cases. Supposing that a minute bubble of steam does commence to form in superheated water, it will grow very quickly, passing almost instantaneously through the range of unstable dimensions; for it is surrounded on all sides with pure water ready for passage into the gaseous condition. But if a minute bubble of hydrogen begins to form upon a supersaturated electrode, it will grow less readily; for the electrode at this point—if composed of a material in which hydrogen is not very soluble—may actually cease to be supersaturated long before the bubble has reached finite (*i.e.*, stable) dimensions. Thus the amount of supersaturation needed for bubble-formation will have to be large.

If the liberation of hydrogen by *diffusion* be prevented, there seems no reason to think that the hydrogen in the supersaturated electrode is out of equilibrium with the hydrogen of the acid. The hydrogen in the electrode is of course out of equilibrium with the gaseous phase above the liquid, which probably contains no hydrogen at all. But at the electrode surface equilibrium is quite possible, and Nernst's equation—suitably modified for the high degrees of supersaturation involved—can be applied. The supersaturation of an electrode with hydrogen is usually a perfectly reversible change. In some instances of oxygen-discharge at anodes, investigated by Luther and others, a

permanent change is produced in the anode by the oxygen, and the p.d.-current curves obtained (1) with increasing, (2) with diminishing p.d. are not congruent. But such cases are to be referred to "passivity."

The idea that overpotential is necessarily an influence making for wastage of energy is quite erroneous. Various reductions which cannot be brought about by hydrogen under atmospheric pressure (whatever catalyst is used) become perfectly possible at an electrode saturated many thousand times over with hydrogen gas. In bringing about an electrolytic reduction of a difficultly reducible liquid a cathode material is selected having a high overpotential, and thus a hydrogen pressure of thousands—possibly millions—of atmospheres is obtained, and reduction effected.

Apart from these considerations, Professor Richards' experiments do not seem conclusive. They are interpreted as proving that there is in the cases under examination no chemical action due to overpotential; the energy consumed through overpotential is accounted for in the heat-evolution. What is really proved is that there is no *lasting* chemical effect. It is, however, quite possible that at those electrodes where the p.d. is depressed or elevated through overpotential, endothermic modifications of hydrogen and oxygen may be temporarily formed. If these are decomposed (yielding the ordinary O_2 and H_2) before the bubbles pass out of the electrolytic cell, which is being used as a calorimeter, the energy previously absorbed in chemical work will be regenerated as heat. The intermediate stage will not be recognized in the thermal measurements.

Professor J. W. Richards, in reply, states that his Note on "Overvoltage" had for its prime object to prove experimentally that the net decomposition voltage *disappearing* in an electrolytic cell was independent of overvoltage, and dependent only upon the net chemical change resulting from the passing of the current. He believes that his experiments, as far as they went, proved this principle. As to what becomes of the overvoltage, how or by what mechanism or sequence it finally appears as heat, is a field for theory or speculation, in which many minds may propose many explanations. If, under any circumstances, a back e.m.f. can be shown to occur equal to the net decomposition voltage plus the overvoltage, then his hypothesis of overvoltage being of the nature of a surface resistance caused by the adhesion of gas bubbles to the electrode would be untenable, and an explanation such as that of Dr. A. J. Allmand would appear more applicable. At any rate, one principle must be borne in mind, viz., that the voltage representing the chemical work done (net decomposition voltage), and which is the minimum voltage necessary to initiate and to continue an electrolytic operation, is a function of the *net* chemical energy change resulting from the passing of the current, and is not conditioned by the voltage of any intermediary or component reactions into which the net chemical reaction may be analysed.

THE DENSITY OF ALUMINIUM.*

By F. J. BRISLEE, D.Sc.

DISCUSSION.

(*Held on Wednesday, November* 26, 1913, MR. W. R. BOUSFIELD, M.A., K.C., VICE-PRESIDENT, *in the Chair.*)

Dr. R. Seligman said that some time having elapsed between the reading of this Paper and the discussion, he felt unable to go into the questions raised in any detail. It appeared that this Paper originated in some remarks of the speaker on Dr. Brislee's former Paper on this subject, although Dr. Brislee had not mentioned this. On that occasion the speaker had drawn attention to the fact that in spite of the immense amount of work done on the metal during rolling and drawing Dr. Brislee found no increase in density. Moreover, as Dr. Brislee also found no increase in density on annealing such hard-worked metal, the latter was not apparently in the amorphous and less dense state described by Beilby in other metals. The present results show that there is in fact an increase in density on annealing, thus removing the anomaly in the author's previous results to which the speaker had drawn attention. Aluminium is thus seen to fall into line with other metals, the hard-worked metal being amorphous and light compared with the denser crystalline annealed metal. These results were important also from the technical point of view, owing to the differences which had been shown to exist in the stability of the hard-worked and annealed metal.

Professor Alfred W. Porter, referring also to the author's observation that the density of aluminium was decreased by working, pointed out that increasing the pressure must always diminish the volume, otherwise the equilibrium at any instant would be unstable. There was a difficulty, however, in the case of the assumed Al cryst. $\longrightarrow$ amorph.; because the transformation persists *after the pressure is removed.* The process was therefore irreversible (assuming that it occurs). This landed one in difficulties, which it was rather hard to express an opinion about. Some information would be useful: Does aluminium become hot when it is rolled? Is anything known about the increase or decrease of the amorphous variety with temperature? He believed that the increase in the *oxidized* surface would be more than sufficient to account for the observed change in specific volume.

Dr. F. J. Brislee (*communicated reply*): In reply to Professor A. W. Porter's questions, the temperature of aluminium certainly rises during rolling. As a rule, however, the rise is not very great, owing to the large rolls acting as coolers, hence it is difficult to say anything about the increase or decrease of the amorphous variety with the temperature. This is also rendered more difficult owing to the partial annealing which the metal undergoes during

* This Paper was published in the TRANSACTIONS (vol. ix., parts 1 and 2) issued in July, 1913, *supra* p. 162.

cooling, and with some metals this is sufficiently great to reduce the mechanical strength. In such cases the metal is cooled in water after passing through the rolls or dies to avoid the "auto-annealing." Finally, there is no increase in oxidized surface as suggested. The specimens referred to in the Paper were all annealed in a non-oxidizing atmosphere and the weights before and after annealing were practically identical, the maximum variations being only a fraction of a milligram. In some cases the specimens were cleaned and polished after annealing to remove any trace of oxide.

AN OXIDIZABLE VARIETY OF NITROGEN.*

By T. MARTIN LOWRY, D.Sc.

DISCUSSION.

(*Held on Wednesday, November 26, 1913,* Mr. W. R. Bousfield, M.A., K.C., Vice-President, *in the Chair.*)

Professor Alfred W. Porter: I happen to have a special interest in any work which brings out the peculiar properties imparted to nitrogen by means of an electric discharge. I have in the last few years made a number of experiments on the figures which appear, after development, upon photographic plates after passing a single discharge over them. The figures which branch away from the negative terminal in air are terminated by tufts shaped like palm leaves, consisting of a number of radiating curved filaments. I have shown that such palm-leaf figures are obtained only in gases containing free nitrogen; nitrogen in compounds does not yield them. But even a trace of free nitrogen (such as is difficult to remove from the sparking chamber) is quite sufficient to give evidence of its presence. Each of the filaments constituting the leaf is of the same shape as the path taken by one of the fragments into which a travelling shrapnel shell breaks when it explodes; and I cannot help thinking that there is a close similarity in the two phenomena. In other words, a very loose aggregate of molecules or atoms or ions is formed in the first place by the discharge. This travels with the discharge and ultimately breaks up explosively. It is possible that the product of the explosion is simply Strutt's nitrogen, which then transforms in a quieter manner into ordinary nitrogen.

The **Chairman** said that he had been familiar with the work done by Dr. Lowry. If he remembered aright it had been found by the use of the oscillograph that the use of an alternating current with a high peak was necessary to get the best results.

* This Paper was published in the Transactions (vol. ix., parts 1 and 2) issued in July, 1913, *supra* p. 189.

THE EMBRITTLING OF IRON BY CAUSTIC SODA.

By J. H. ANDREW, M.Sc. (Research Fellow and Demonstrator of Metallurgy), the University, Manchester.

(*A Paper communicated to the* TRANSACTIONS *of the Faraday Society, December*, 1913.)

Some time ago the author's attention was drawn to the peculiar although not uncommon occurrence of extreme brittleness in an iron tube which had been in use in a caustic soda concentrator. The tube was one of many which had broken off during the repairing of the concentrator, the breaking taking place at the expanded ends of the tubes.

Upon bending a small section of the tube, fracture readily occurred through the crystalline portion, the piece being only held together by a thin layer of the original fibrous material that had remained unaltered. The fracture was highly crystalline, the crystals being extremely large and brilliant.

An examination of the edge showed that fracture had taken place through the junction of the ferrite grains, and not across the grains themselves. A photomicrograph of this fracture is shown in Fig. 1.

Although large crystallization is usually associated with brittleness, the size of the crystal grains is not the predominating factor, the mechanical properties of the metal being dependent rather upon the cohesion of the grains and of the amorphous cement which binds them together.

The structure of a polished and etched specimen of the crystalline portion of the tube showed a somewhat curious appearance. Not only were the ferrite grains very large, but their boundaries were considerably thicker than is normally the case. Each grain was covered with a network of peculiar markings, which could only be photographed by arranging the specimen so as to be slightly out of focus or by using oblique light.

The thick cell walls between the grains and the grain markings are shown in Fig. 2.

The deteriorative effect of caustic soda upon iron and mild steel has been recognized for some time, but no definite explanation of the phenomena based on experimental evidence has yet been put forward; experiments were therefore carried out with the idea of throwing further light upon this problem.

Mr. Stromeyer,[1] in a paper on "The Ageing of Mild Steel," writes as follows: "N came out of a cracked boiler in which caustic soda had been concentrated. At the time of writing the first paper it seemed unreasonable to suppose that a caustic liquor should in any way affect steel, but the author's attention has recently been very forcibly drawn to this matter, and it appears that if the concentration of the soda liquor is allowed to proceed beyond 100° Twaddle, not only does the mild steel become brittle in quality, but tubes and plates crack and rivet-heads fly off. Rivet-heads even fly off in steel tanks in which cold caustic soda of over 100° Twaddle is stored. Hot caustic soda corrodes mild steel, a rod which was recently exposed to

316 a

FIG. 1.

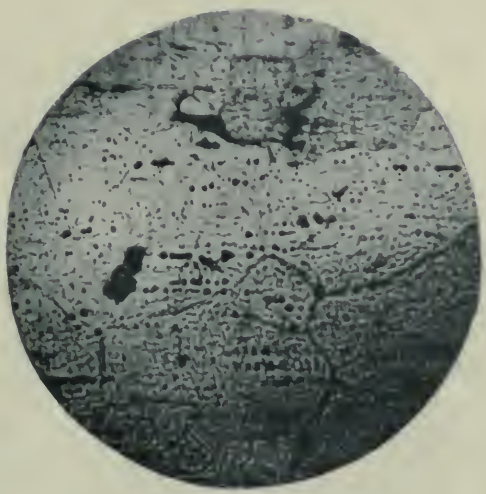


FIG. 2.

this influence being reduced in diameter at the rate of about 1/10 inch in fourteen days' exposure. It has been suggested that air which in this case at least had access to the liquor, parts with some of its oxygen to the iron, and that an iron salt of soda, perhaps ferrate of soda, is formed, which is soluble in solutions of soda and water, but not in molten caustic soda; but until the matter has been cleared up, one should not reject the possibility that in the presence of caustic soda and iron, water splits up, the oxygen forming ferric oxide or acid, which combines with the caustic, whilst the hydrogen is occluded by the iron metal. This would account for the extraordinary brittleness which is imparted to mild steel vessels in which caustic soda liquor is being concentrated, more particularly as this brittleness makes its appearance chiefly if not exclusively in closed vessels in which air is not admitted, and where corrosion, if at all active, is very slight."

Mr. Stromeyer, in a later report, drew attention to the fact that corrosion of iron by caustic soda takes place when the caustic soda is allowed to exceed 90° Twaddle, and that brittleness and corrosion only occur when the metal is in tension, metal in compression, or metal which is neither in tension nor compression not being affected.

Mr. Stromeyer's suggestion that the brittleness might be due in some way to the occlusion of hydrogen is extremely interesting, and, in view of the deteriorative effect that this gas is known to have upon iron, not at all improbable. It is known for instance that iron and steel when quenched in water from a high temperature decompose the water, and this, as Richards has shown, is followed by occlusion of hydrogen.

Again, the brittleness of an iron wire after dipping in acid is always explained upon the assumption that hydrogen is absorbed by the iron.

Roberts-Austen[2] has shown that when iron is made the negative electrode in a battery decomposing acidulated water, a part of the hydrogen formed at the cathode is occluded by the iron, the metal after this treatment giving the well-known hydrogen points in a cooling curve determination.

Sieverts[3] has shown that iron begins to occlude hydrogen at a temperature of about 400° C. With increase of temperature the quantity of gas picked up by the metal increases, the increase being almost a linear function of the temperature up to 850°; at 850° there is a break in the temperature-concentration curve, the concentration showing a rapid increase up to 900°, after which the curve again becomes linear up to the melting-point. At the melting-point the concentration rapidly increases. The break in the curve between 850° and 900° is undoubtedly connected with the transformation point in the iron, hydrogen being more soluble in the gamma modification than in the alpha. Although Sieverts has proved that solution of hydrogen in iron is almost negligible below 400°, it must be remembered that his experiments were carried out with molecular hydrogen, atomic hydrogen, as Roberts-Austen has shown, being occluded by iron at ordinary temperatures, and it is in this state that hydrogen must exist previous to its evolution as molecular hydrogen, from the metallic surface in the caustic soda experiments.

The first method of attacking this problem to suggest itself was to estimate the quantities of hydrogen before and after treatment with caustic soda. The methods of estimating gases in steel are, however, not sufficiently delicate to be of any value when it is considered that exceedingly minute amounts of hydrogen may produce a relatively great effect.

In order to obtain some idea as to the extent of the action of caustic soda upon iron and steel, and of its effect upon the structure of the metal, specimens of wrought iron and of a 0·5 per cent. carbon steel were heated in

a concentrated aqueous solution of caustic soda at 100° C. The specimens were immersed in soda, contained in a flask fitted with a reflux condenser heated by means of a steam bath. Contact between the air and the soda solution was purposely effected. Two samples of wrought iron were taken, having a thickness of approximately 1 mm.; one of the specimens was rough filed, and the other one highly polished, both on the large flat surfaces and upon the edges. The steel specimens were circular discs 1 in. in diameter and about 1·5 mm. thick.

Both polished and unpolished specimens were employed in order to determine the effect of surface, the surface of the polished samples being less than the surface of the unpolished specimen, and according to Dr. Beilby,[4] composed of amorphous material, quite distinct in properties from the crystalline metal underlying it.

The results obtained were as follows:—

Original weight of polished iron	... ...	5·5508 grams
„ „ unpolished iron	... ...	4·7890 „
„ „ polished steel	... ...	6·5512 „
„ „ unpolished steel	... ...	5·2235 „

After four days a white precipitate was formed.

On the seventh day the solution was renewed owing to the formation of silica by interaction between the soda and the glass. A small bar of wrought iron which had been added for testing purposes was found to be quite brittle, whilst the polished iron had developed a crystalline appearance.

On the tenth day the wrought iron had become highly crystalline, and a large quantity of precipitate had formed.

On the twentieth day another small sample of wrought iron was withdrawn and found to be brittle, breaking with a small tap of the hammer; the fracture was highly crystalline. The crystals shown upon the surface of the polished iron had increased in size, whilst the unpolished sample was also highly crystalline.

The only difference indicated by a micro-examination of the wrought iron test bars was an increase in the size of the ferrite grains, this increase being very considerable.

The outward appearance of the steels remained unchanged, excepting that the surfaces showed a tendency to become dull.

During the experiment a gas was evolved which was proved to be pure hydrogen. All the specimens were covered with bubbles of gas, and, after stirring the liquid and thereby freeing the gas, fresh bubbles gradually formed.

After heating for twenty days the specimens were taken out, washed in water and alcohol, dried, and then weighed.

The losses in weight given as percentage loss per day are as follows:—

	Loss per Cent. per Day.
Polished wrought iron	0·08478
Unpolished „	0·1868
Polished steel	0·02377
Unpolished steel	0·08796

The effect of surface is very manifest in these figures, the polished iron corroding at less than half the rate of the unpolished, whilst the polished steel corroded at only one quarter the rate of the unpolished.

A comparison of the polished and unpolished sections of the wrought iron

and of the steel indicates very markedly the greater corrodibility of the former.

The specimens were then immersed in fresh solution and allowed to remain for fifty days, the solution being renewed from time to time.

Crystalline development continued, and at the end of this period the crystals in the originally polished iron in many cases exceeded 1·5 mm. in diameter.

The losses in weight during this period were as follows :—

	Loss per Cent. per Day.
Polished wrought iron	0·1549
Unpolished „	0·1658
Polished steel	0·0249
Unpolished steel	0·0409

The most noticeable points to be observed from these figures are as follows : (1) The rate of corrosion excepting in the case of the polished iron has decreased ; (2) the rate of corrosion of the polished and unpolished iron have become nearly equal, this being no doubt due to the area of the two specimens becoming nearly equalized by the action of the soda, the amorphous surface of the polished specimen by this time having become crystalline ; (3) the corrosion of the iron is much greater than that of the steel. The steel showed no signs of crystallization, and its surface had by this time become somewhat blackened.

The specimens were again immersed in the soda solution, but during this period the tendency of the specimens to become covered with a black deposit extended to the wrought iron. This black deposit, which is in all probability Fe_3O_4, by protecting the surfaces from interacting with the soda renders these results of less value. In the case of the two steel specimens the deposit was sufficiently dense to effect an increase in weight.

After twenty-four days the increase or decrease in weight was as follows :—

	Loss or Gain in Weight per Cent. per Day.
Polished wrought iron...	0·0200 loss
Unpolished „	0·0614 „
Polished steel	0·0205 gain
Unpolished steel	0·0184 „

That a considerable decrease in the rate of corrosion is only to be expected when the surfaces are thus protected. The black deposit was exceedingly tenacious and could only be removed by abrasion.

Further treatment effected a still further increase in weight, not only of the steel but also of the wrought iron.

The increase or decrease in weight after a further treatment lasting ten days is as follows :—

	Loss or Gain per Cent. per Day.
Polished iron	0·0030 gain
Unpolished iron	0·0145 loss
Polished steel	0·0046 gain
Unpolished steel	0·0042 „

One interesting feature in connection with these values is that just as the polished specimens showed the least tendency to corrode, their gain in weight upon prolonged immersion is greater.

After this treatment the specimens were broken in two. The polished and unpolished wrought iron both bent double before fracture occurred, although the fractured surfaces were bright and highly crystalline. The prolonged treatment must, therefore, have reduced the brittleness shown by testing the small sample bars, to be produced during the initial stages of the immersion.

The steels, whilst exhibiting no alteration in their crystalline nature, broke at an angle of 45°, the fracture being fibrous as it was originally. One half of the broken sections of the wrought iron, and of the steel, was then cleaned with emery and returned to the soda.

The losses in weight are as follows :—

After 21 days' treatment—

	Loss per Cent. per Day.
Wrought iron	0·1240
Steel (1)	0·1253
Steel (2)	0·1049

After a further 13 days' treatment—

	Loss per Cent. per Day.
Wrought iron	0·01815
Steel (1)	0·0778
Steel (2)	0·0713

The interesting feature of these last results is that, whereas upon exposing a clean surface to the caustic soda corrosion sets in at a normal rate, the rate of corrosion rapidly decreases with time, the corrosion of the wrought iron after the second immersion being reduced to a minimum, whilst the values for the steel also show a sudden decrease.

The conclusions arrived at from these experiments may be summarized as follows :—

(1) Wrought iron is corroded more rapidly than a 0·5 per cent. carbon steel, when immersed in a concentrated solution of caustic soda at 100° C. This may be attributed to two causes, in the first case, whereas pure iron contains 100 per cent. ferrite, the ferrite areas in a 0·5 per cent. carbon steel occupies only 50 per cent.; if the iron carbide is less effected by the soda than pure ferrite, this difference becomes obvious. Secondly, whereas the wrought iron preserves a bright surface for a considerable length of time, the surface of the steel becomes more rapidly coated with a protective deposit.

(2) The polished specimens corrode much more slowly at first than those which have been unpolished. This may be attributed either to the resistance of the amorphous phase to the action of soda being greater than that of the crystalline, or to the uniformity of the polished surface, the homogeneous character of which prevented any electrolytic action from setting in. Owing to the impossibility of obtaining a perfectly polished specimen coated with a complete layer of the amorphous material, electrolytic action could not entirely be prevented; moreover, when once the amorphous surface had been partially destroyed a state similar to that existing in the unpolished sample is quickly arrived at.

It must also be taken into account that a polished metal necessarily presents less surface than an unpolished specimen of similar dimensions.

(3) A 0·5 per cent. carbon steel becomes coated with a black deposit after a not very prolonged immersion in caustic soda. A similar deposit eventually forms upon the surface of the iron, but the iron retains its brightness for a considerably longer period than the steel.

The black deposit, which is in all probability an oxide of iron Fe_3O_4, by protecting the metal from the action of the soda, not only prevents loss in weight by corrosion, but is the cause of an actual gain in weight.

(4) A white precipitate invariably forms during the treatment. This precipitate upon analysis was found to contain sodium, iron, and silica.

The silica is undoubtedly due to the formation of sodium silicate by interaction of the soda and the glass vessel.

After deducting the sodium necessary to combine with the silica to form sodium silicate, an analysis showed the iron content to be 20 per cent.

The precipitate is most probably sodium ferrate in various stages of decomposition, the precipitate becoming brown in long standing owing to the formation of hydroxide of iron.

(5) Evolution of gas which was afterwards shown to be pure hydrogen occurred at the surfaces of the iron and steel specimens.

This evolution of hydrogen has a most important bearing upon the question of corrosion and embrittling of iron by caustic soda and will be dealt with at some length.

When it is considered that the crystallization effected by this treatment occurs not only on the surface of the metal, but throughout the mass, it is evident that the agent which brings about this complete molecular re-arrangement must be extremely penetrating in its action.

The possibility of an aqueous medium entering into the pores of the metal and finding its way to the centre need hardly be considered, nor can heat alone be responsible, specimens kept in oil for several months at 100° C. exhibiting no change whatever.

The fact that the brittleness produced during the first few weeks of treatment ultimately disappears and malleability is again restored, is important, and points to a more mobile agent than either liquor or solid.

It is extremely probable that hydrogen is the cause of the phenomena ; its penetrating effect upon metals has long been known. Not only will it diffuse through metallic iron, but it is occluded by this metal in quantities varying with the condition of the gas and the metal itself. The evolution of hydrogen at the surface of the metal is particularly favourable to its occlusion, the gas being in the nascent state at the moment of its formation, the tendency for it to go into solution or combination with the iron is at a maximum.

Having established the theory of hydrogen absorption, the next questions to be considered are (1) the actions evolved in the production of the hydrogen, (2) the mechanism of the recrystallization of the metal.

Beilby has shown that a metal which has been strained in the cold is duplex in nature, consisting of crystalline grains cemented together by thin films of amorphous metal.

Rosenhain,[5] however, believes that this amorphous cement exists in all metals cooled from the liquid state, and that the mechanical properties of the metals are dependent upon it. Rosenhain's theory receives strong support and is now generally accepted.

A two-phase system of this character when immersed in a solution of an electrolyte will constitute a self-contained cell ; the potential difference between the amorphous and the crystalline material will cause a current to flow, and electrolysis to follow.

In view of the fact that an increase in the concentration of the soda increases both the rate of corrosion and the quantity of hydroxyl and sodium ions present, the most probable explanation of the reaction is that represented by the following equations.

In the first place the iron will go into solution at the anode, as ferrous iron, with two positive charges—

$$4Fe + 8\oplus = 4\,Fe^{++} \text{ at anode.}$$

This will then be oxidized by the oxygen in solution to ferric iron, giving rise to the production of hydroxyl ions—

$$4Fe^{++} + O_2 + 2H_2O = 4Fe^{+++} + 4\bar{O}H.$$

The ferric iron will then react with the hydroxyl ions produced and with the sodium and hydroxyl ions from the sodium hydrate, with the formation of sodium ferrite, and liberation of hydrogen at the cathode.

$$4Fe^{+++} + 4\bar{O}H + \underbrace{4\bar{O}H + 4\dot{N}a}_{} = \underbrace{4Fe\dot{O}_2 + 4\dot{N}a}_{} + 8\dot{H},$$

$$8\dot{H} = 4H_2 + 8\oplus \text{ at the cathode.}$$

The sodium ferrite will be in solution, unless it becomes further oxidized to sodium ferrate.

It will be seen that in this suggested explanation the presence of oxygen in solution is required.

It might be thought, therefore, that the reason for a decrease in the rate of corrosion with time was due to all the oxygen being used up. Constant changes of the soda solution and exposure of the metal to the air during weighing show conclusively that this cannot be the case.

It is impossible to state definitely the polarity of the two phases of the iron. It is, however, sufficient to know that hydrogen is evolved in the atomic state, and in this condition is rapidly occluded by the metal.

The question now to be considered is, will the gas be absorbed by the crystalline phase, the amorphous phase, or by both, and how does this absorption bring about recrystallization and brittleness.

Recent experiments carried out by the author[6] in conjunction with Dr. Holt throw considerable light on the question of gaseous absorption by amorphous and crystalline metals. The metal experimented with was palladium, which can readily be obtained in the normal crystalline form and as amorphous palladium or palladium black. It was shown that whilst amorphous palladium occludes hydrogen with great avidity, and with evolution of a considerable quantity of heat, the rate of occlusion of this gas by palladium foil is extremely slow.

If a piece of palladium in the form of foil or fused mass be heated strongly in the air in order to oxidize the surface, the metal is rendered extremely active towards hydrogen.

The first effect of the hydrogen is to reduce the oxide of palladium, the reduction taking place at room temperature with considerable evolution of heat. The reduction of the oxide at once gives rise to the amorphous metal, and a specimen so constituted—namely, a crystalline metal coated with an amorphous film—rapidly occludes hydrogen gas. Hydrogen is first condensed on the amorphous surface, and then rapidly diffuses into the interior of the mass, until equilibrium has been attained between the interior and the condensed surface layer. The amorphous film acts therefore as a vehicle for the transmission of the hydrogen into the interior.

Whereas the hydrogen may be completely pumped from the amorphous material at ordinary temperatures (as has been shown by employing pure palladium black), it is necessary to raise the temperature in order to extract the gas completely from the crystalline mass.

If, therefore, a specimen containing both varieties of the metal, previously saturated with hydrogen, be placed in vacuo, the gas condensed upon the surface by the amorphous material will be evolved immediately, whilst diffusion of gas from the interior takes place slowly, and will continue until equilibrium has been established.

Palladium saturated with hydrogen exhibits no outward difference. If, however, hydrogen be continually added and then extracted, the metal becomes crystalline and highly brittle, whilst its power of rapidly occluding hydrogen is increased. Such treatment, by continually bringing about a molecular disturbance, gives rise to the production of the active phase, that is to say, the amorphous material.

Another observation which has an important bearing upon the problem of gaseous occlusion, is that if sufficient time is given for the gas to penetrate right into the interior of the metal, extraction of the gas requires longer time or a higher temperature to be completely brought about.

It stands to reason therefore that the thicker the specimen, the more difficult it is to pump out the gas. It is not definitely known whether an amorphous or finely divided metal will occlude a greater volume of gas than the massive and crystalline metal, but finely divided iron does show greater readiness to occlude gases than the metal in a massive form.

If the vitreous or amorphous metal has a constitution similar to that of a liquid, that is to say, is considered as a supercooled liquid, the probability is that the solubility of hydrogen in this phase will be of the order of the solubility of the gas in the liquid metal, which Sieverts has shown to be much greater than its solubility in the solid. This applies not only to iron but to many other metals.

Taking it for granted that the proof of the solubility of the atomic hydrogen in the iron caustic soda reaction has been established, the question now to be considered is the effect of the occluded hydrogen.

It is probable that in the first instance hydrogen is absorbed rapidly by the amorphous layers between the crystals and diffuses along the paths occupied by this phase between the crystal grains. The immediate effect will be to cause an expansion in the amorphous cement, forcing the ferrite grains apart and depriving them of their binding material. Not only will the destruction or alteration in the character of this cement produce a breakdown in the crystalline cohesion, but by forcing the allotriomorphic grains apart, will facilitate recrystallization of the grains themselves.

When the concentration of the hydrogen in the amorphous metal has reached a certain value, it will diffuse from this into the crystalline mass itself, causing a mechanical disturbance and probably recrystallization of the amorphous phase, and producing finally two forms of iron saturated with hydrogen.

The potential difference between these two phases, namely, amorphous and crystalline metal saturated with hydrogen, will now depend not upon the two varieties of the metals, but upon the hydrogen concentration in them; and there is every reason to suppose that it will be less than was formerly the case. The combination of these two phases will now constitute a hydrogen cell, and owing to the low potential difference and polarization by the gas electrolytic corrosion should be reduced to a minimum.

According to this view it would be expected that the corrosion of iron by caustic soda should gradually decrease with time, or in other words, by allowing sufficient time for occlusion of hydrogen the corrosion should be reduced to a minimum. Experiments show this to be the case, the unpolished iron and steel exhibiting a decreasing tendency to corrode, as the time of immersion is increased.

This is most strikingly evident in the experiments (5) and (6). Before these experiments the specimens had remained in soda for over 100 days, and would, therefore, be expected to contain a relatively large amount of hydrogen. They were reground in order to expose a fresh surface; any hydrogen in the immediate neighbourhood of the surface would thus be liberated or oxidized. The first effect of the caustic soda treatment would then be to hydrogenize this new surface, and the corrosion would be quite normal. Further treatment, however, produced but little corrosion.

It may be concluded from this that when once the new surface had been attacked the rate of corrosion suddenly decreased, the interior being more or less saturated with hydrogen by the previous treatment lasting over 100 days.

If hydrogen gas were to act in the manner suggested it would be expected that iron originally saturated with hydrogen would corrode at a considerably less rate than iron free from this gas. Indeed, if polarization were complete, corrosion should not occur at all.

In order to test this point the following experiments were carried out.

Three strips of electrolytic iron 1 mm. thick were taken and treated as follows:—

(1) One strip was heated for several hours at 900° in a stream of hydrogen and cooled in that gas.

(2) The second was heated in hydrogen, cooled in hydrogen, and then heated to 1,000° in vacuo, and cooled in vacuo. In passing, it might be mentioned that after this treatment the metal exhibited the usual intercrystalline brittleness and large crystal grains.

(3) The third specimen was untreated.

The weights of the strips were as follows:—

A. Untreated ... ... 5·7780
B. Heated and cooled in hydrogen and then in vacuo ... 4·0090
C. Heated and cooled in hydrogen ... ... 6·0520

The strips of metal were bent in the form of a small cylinder so that they just fitted into the end of an inverted gas-collecting tube. The gas tube containing the cylinder was then placed in a concentrated solution of caustic soda contained in a wide tube; after the caustic soda had been sucked up through the gas tube by means of the stop-cock at the top, and all air carefully expelled, more caustic soda was added in the outer tube, and this was covered with a layer of oil to prevent access of air. This combination was then placed in a water-bath and a temperature between 90° to 100° C. maintained. A sketch of the apparatus is given in Fig. 3.

The samples were weighed at intervals of 15, 13, 7, and 16 days respectively, the caustic soda being renewed after each weighing.

The percentage loss in weight per day is tabulated below.

Percentage Loss in Weight per Day.

Sample.	Period of Treatment in Days.			
	15	13	7	16
A	0·01152	0·02134	0·08690	0·04910
B	0·00580	0·1680	0·07063	0·02979
C	0·00440	0·00954	0·00889	0·02174

These results furnish valuable evidence as to the correctness of the statements made with regard to the action of hydrogen.

It is seen that the corrosion of the two samples A and B gradually increases as the surface exposed by recrystallization and adsorption of the amorphous material becomes greater; after a certain period of time corrosion is at a maximum, and further treatment produces a decrease in the rate; this

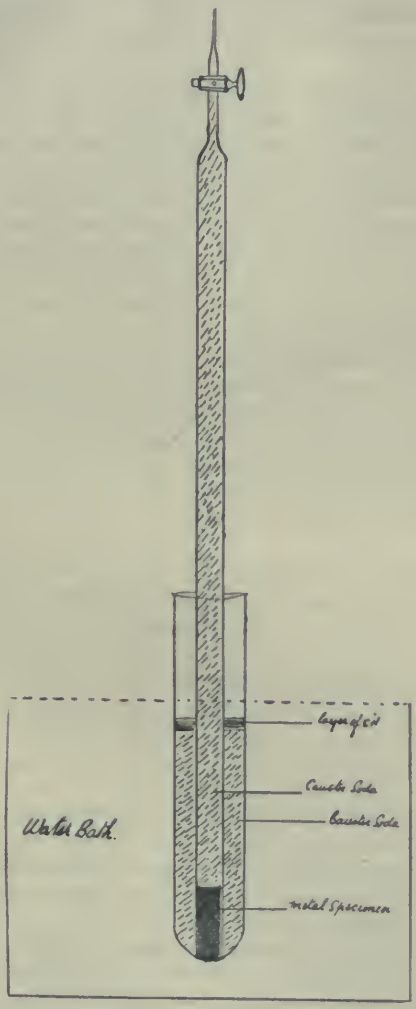


FIG. 3.

decrease will correspond with the saturation of the amorphous layer, and diffusion of hydrogen from it into the crystalline.

The results obtained with specimen C are as exactly as would be expected, the degree of corrosion having been considerably lessened by saturating the specimen with hydrogen.

It must be taken into account, however, that the gas has been heated in molecular hydrogen so that it will be unsaturated with respect to atomic

hydrogen, or, in other words, hydrogen in the atomic state would still be occluded.

Owing to the small difference of potential due to its occlusion of molecular hydrogen the reaction takes place extremely slowly at first ; if, however, by any chance molecular movement occurs within the specimen (and such was the case in these experiments, the metal becoming more crystalline even although corrosion was feeble), a greater surface will become exposed to the hydrogen and further occlusion will take place. This accounts for the increase of corrosion with time as shown by the last sixteen days' treatment of the specimen.

It is interesting to consider Mr. Stromeyer's results in the light of the theory now put forward. Mr. Stromeyer states that whereas the metal in tension is rapidly affected by soda, iron in compression remains unaltered.

In view of the fact that brittleness resulting from this treatment is due to the forcing of the ferrite grains apart by the expansion of the amorphous material resulting from occlusion of hydrogen, any force, such as a compressive force, will tend to oppose this expansion, and therefore to prevent the crystals from being forced apart. Metal in tension, however, will tend to produce the opposite effect, the natural tendency for the crystal grains to be drawn apart facilitating the reaction.

An attempt was made to collect the gas evolved from the different samples during treatment. The silica which resulted from the action of the soda on the glass rose to the top of the collecting vessel, and bubbles of gas in rising were mechanically held by the gelatinous precipitate, so that it was impossible to extract the entire volume of hydrogen.

The volumes are given, however, as an indication of the relative amounts of hydrogen evolved.

Sample.	No. of Experiment.			
	1	2	3	4
A.....	2·9 cc.	4·8 cc.	1·0 cc.	1·0 cc.
B	2·2 „	1·8 „	0·5 „	0·5 „
C.....	1·0 „	0·3 „	0·5 „	0·5 „

There is no direct relation between the volume of gas and the corrosion, the volume evolved being dependent upon the volume occluded.

The relatively large volume evolved by the untreated iron is due most probably to the original material containing atomic hydrogen, requiring therefore less hydrogen for its saturation.

The gas was analysed and found to be pure hydrogen.

In a paper recently published by Dr. Stead and Professor Carpenter[7] upon the crystallizing properties of iron, it was shown that the recrystallization of electro-deposited iron is brought about by a method quite inapplicable to iron made by other means.

The author's conclusions were as follows :—

By heating electro-deposited iron above the A_{c3} point, and then cooling below A_{r3}, relatively enormous crystals are formed.

Very prolonged heating above A_{c3}, followed by slow cooling, does not result in the formation of coarse crystals.

Once the coarse crystals are formed they cannot be destroyed, except by cold mechanical work or by heating above A_{c3}, followed by quenching. The

very heat treatment that produces coarse crystals in the electro-deposited irons refines wrought iron and mild steel which have been rendered coarsely crystalline by close annealing between 700° and 800° C. On the other hand, annealing between 700° to 800° has no effect in coarsening the structure of electro-deposited iron which has been refined by cold mechanical work. In these respects, therefore, the behaviour of electro-deposited iron is precisely opposite to that of wrought iron and mild steel.

The writer's experiments upon iron and caustic soda have clearly shown that hydrogen, upon being occluded by iron, immediately gives rise to the production of large crystals and brittleness.

Moreover, if an electro-deposited iron be heated in hydrogen and then heated to 1,000° C. and cooled in vacuo, the resulting metal will not only be excessively crystalline, but brittle enough to crush in the hand.

The important difference between electro iron and wrought iron is that whereas the former is made under conditions which favour the occlusion of atomic hydrogen, the wrought iron, and also the mild steel, will in all probability contain but a small amount, and such hydrogen as exists will be in the molecular state.

It has been shown that iron gives up the greater part of its hydrogen as the temperature passes through that of the critical ranges.

This is to be expected, for at the critical temperature not only is there a momentary breakdown of the molecular structure, thereby greatly facilitating the escape of any gas, but there is also a change in the phase, from gamma to alpha, these two phases differing in their capacity to occlude hydrogen, the gas being more soluble in the gamma phase than in the alpha.

It is not contended that hydrogen *per se* is the cause of crystallization, but rather that it is due to the evolution or occlusion of hydrogen effecting a molecular disturbance.

This is borne out by the results obtained on cooling electro iron in hydrogen, the metal after this treatment exhibiting no excessive crystallization or brittleness, the tendency for hydrogen to be evolved being reduced by a pressure of that gas on the exterior of the metal during the cooling.

Moreover, in order for a molecular disturbance to be brought about during the passing of the metal through the critical range, it is not necessary that it should be saturated with hydrogen.

When it is considered that the movement of hydrogen molecules are able to bring about recrystallization at so low a temperature as 100° C., it is highly probable that at the critical points the effect will even be greater, and larger crystals produced.

The suggestion is therefore put forward that the crystallization of electro-deposited iron as it cools through the critical temperature is due to the evolution of hydrogen, and quenching above the critical temperature, by not allowing time for this molecular disturbance to take place will prevent recrystallization.

Just as hydrogen accentuates crystallization under these conditions, so will it deter crystallization when the conditions are different, and the reason for the failure of the iron to crystallize upon annealing below the A_{c3} point (and this should normally occur) may be attributed to the occluded hydrogen acting as an impurity, preventing crystallization.

This impurity, namely hydrogen, is at a minimum in wrought iron and mild steel, thus allowing them to behave in a normal manner, that is to say, to recrystallize when heated between 700° and 800° C.

Above 800° there is a probability that gamma iron begins to be formed. Indeed, Sieverts's temperature-hydrogen concentration curve shows a break

not at 900°, but beginning at a temperature below 850°, an indication of the gradual formation of a phase having a greater solubility for hydrogen than alpha, that is to say, gamma iron.

That gamma iron is formed at this temperature upon heating has never been suggested, but in consideration of the work of Benedicks and Carpenter it is not at all untenable, and receives support from the work of Sieverts just mentioned.

If gamma iron begins to form at 800°, the refusal of wrought iron to crystallize at temperatures above this will be obvious.

The extreme brittleness of electro iron which has been cooled in vacuo from a high temperature is not necessarily due to the absence of amorphous material, as this phase would be increased in quantity by evolution of hydrogen. The evolution of gas will, however, give rise to the formation of very spongy metal around the crystal boundaries, with the result that the cohesion of the grains will be exceedingly weak.

The reason for the crystallization of a thin strip of electro iron and the non-crystallization of a thicker strip follows from what has been said in respect of hydrogenized palladium, the thicker the metal the greater will be the difficulty in extracting the gas, and accordingly the smaller effect.

The passivity of iron following its immersion in caustic soda or potash can readily be explained upon the foregone hypothesis. The iron after immersion is charged with hydrogen, the concentration of the gas in both the amorphous and crystalline phases depending upon the strength of the soda solution and the time of treatment.

Whereas previous to being charged with hydrogen, the metal, owing to its duplex nature, constituted a self-contained cell producing an electrolysis when immersed in an electrolyte, the moment it becomes charged with hydrogen the potential difference between the two phases will be dependent upon their respective hydrogen concentrations. It may be concluded from the experiments that as the hydrogen increases, the potential difference decreases, the metal when saturated constituting a hydrogen cell and thereby becoming inactive. If, however, a discharge of the occluded hydrogen should take place, that is to say, if the gas be expelled, oxidized, or in any way affected, the metal will again resume its active state.

It was noticed that whilst a specimen which had been rendered inactive by soda would remain bright in the air for a considerable time, rusting eventually set in. This can easily be accounted for, since although the pressure of hydrogen in the metal is considerable, the partial pressure of the hydrogen in the atmosphere is negligible, so that although the gas may exist in the metal as a true solution the dissociation pressure of this solution would produce decomposition at the immediate surface, and electrolytic corrosion would set in.

Conclusions.

Wrought iron when immersed in a concentrated solution of caustic soda corrodes slowly, becomes highly crystalline, and eventually brittle.

It has been suggested that the corrosion is due to the iron being constituted of two phases, a crystalline and an amorphous phase.

When a duplex metal of this nature is immersed in an aqueous solution of caustic soda, electrolysis sets in, iron going into solution at the anode and hydrogen being liberated at the cathode, whilst sodium ferrite is formed in the solution.

The hydrogen, after giving up its charge at the cathode, is partially liberated and escapes and partially occluded by the metal.

It is the occlusion of, and diffusion into, the interior of this hydrogen which brings about crystalline growth and brittleness in the metal, the hydrogen being first absorbed by the amorphous plate which exists between the crystals, thereby forcing the crystals apart.

When both the amorphous and the crystalline metal have become saturated with hydrogen, or partially saturated, the potential difference between the amorphous and the crystalline metal will drop, with the result that the rate of corrosion will diminish.

The initial brittleness of the iron decreases with time, an equilibrium between the metal and the gas being finally established.

The brittleness is due rather to the molecular rearrangement brought about by occlusion or evolution of hydrogen than to the mere presence of hydrogen in solution.

The passivity of iron produced by immersion in caustic soda is due to the small potential difference between the hydrogenized amorphous and hydrogenized crystalline phases.

Precisely the same effects were noticed when using electro-deposited iron. If, however, the metal be previously charged with hydrogen, the rate of corrosion is less, proving that the rate of corrosion is dependent upon the hydrogen content.

The recrystallization of electro-deposited iron upon cooling slowly through the A_{r_3} point is explained upon the basis of hydrogen evolution ; as the iron cools through the critical point, the evolved hydrogen affecting a recrystallization of the metal.

A 0·5 per cent. carbon steel is affected to a much less degree by caustic soda solution.

In conclusion, the author wishes to express his indebtedness to Professor Carpenter for supplying him with the electro-deposited iron, and also for the kind interest which he has taken in the investigation.

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REVIEWS OF BOOKS.

Metallography. By C. H. Desch, D.Sc. Second edition. (London, 1913: Longmans, Green & Co. Pp. x + 431, with 14 plates and 108 diagrams. Price 9s. net.)

The call for a second edition of Dr. Desch's "Metallography" has come very quickly and testifies to the popularity of an excellent text-book. The chief additions are found in the sections on the "Physical Properties of Alloys" and on "The Metallography of Iron and Steel." The equilibrium-diagram of the carbon-steels still remains the subject of controversy; the diagram of Upton, reproduced in the new edition of the book, is one of the latest to be put forward, though it may be doubted whether it will be by any means the last. The new edition, like its predecessor, may be commended without hesitation as the best book on the subject that has appeared in the English language.

Organic Chemistry for Advanced Students. Vol. II. By Professor J. B. Cohen, Ph.D., B.Sc., F.R.S. (London, 1913: Edward Arnold. Pp. viii + 428. 8vo. Price 16s. net.)

Those who have read Vol. I of the author's "Organic Chemistry" will extend a hearty welcome to the new volume. To those persons, however, who are not in this position the present work will make no such appeal, for it is incomplete in itself, there being a large number of references to facts mentioned in the older book. The chapter on condensation has been transferred *en masse* from the first volume, but considerable and valuable additions, notably Sabatier and Senderens' method of reduction, have been made to it. A large portion of the second volume is devoted to the completion and bringing up-to-date of certain chapters in the first volume. Consequently it would have been much more satisfactory if a revised edition had appeared, so as to include, in addition to the original contents, the subject matter mentioned above, as well as the remaining portion of the book which is completely new. The fact that the first edition was by no means unwieldy is an additional reason in favour of this. The rest of the book contains material which has been adequately dealt with by Smiles in his "Physical Properties and Chemical Constitution," and by Mellor in "Chemical Statics and Dynamics," but of course there are many new observations which have been included in Professor Cohen's new book, and which do not appear in either of these works. The portion devoted to physical properties and their relation to constitution has been enriched with diagrams of the apparatus used and of the absorption spectra of the compounds dealt with, and this adds much to its value.

It in no way detracts from the merits of the book that the contents inspire a great deal of thinking, since in many cases the theories propounded cannot be taken for granted without reflection. Mention must be made of Dr. Dawson, to whom the useful chapter on the "Dynamics of Organic Reactions" is due. The contents of the book are treated very fully, though

concisely. Mistakes are more numerous than would have been expected, and one is surprised to find chlorine referred to as an electropositive element. As a text-book the new volume will undoubtedly prove to be almost, if not quite, as useful to students as did the well-known earlier treatise.

A Text Book of Quantitative Chemical Analysis. By ALEXANDER CHARLES CUMMING, D.Sc., and SYDNEY ALEXANDER KAY, D.Sc. (London, 1913: Gurney & Jackson. Pp. 382, including Appendix and Index. Price 7s. 6d. net.)

This work, according to the Preface, is intended chiefly for University and College students, and the authors have dealt with the subject, with few exceptions, in a careful and scientific way. It is divided into ten parts, which include, amongst others, sections devoted to Volumetric Analysis, Gravimetric Analysis—this with a subsection on Electrolytic Methods for Copper, Cadmium, Nickel, and Lead—Colorimetric Analysis, and Systematic Quantitative Analysis. In the latter, the elements and radicals are arranged alphabetically, with many references to other parts of the book for particular methods of analysis. There are also chapters on Gas Analysis, with the use of the Hempel and Orsat Apparatus, and the Lunge Nitrometer, and a section on Water Analysis, which has its usefulness considerably enhanced by a note on the Significance of Results which is appended. This does not by any means exhaust the subjects dealt with, but will serve to give an idea of the general arrangement of the work. The chapter on Electrolytic Analysis will no doubt receive revision in subsequent editions, particularly the statement that, under the conditions given, cadmium is deposited on the *anode* from a solution of potassium cadmium cyanide, and the reason advanced for this, namely, that the cadmium in the potassium cadmium cyanide forms part of the complex acidic radical, is hardly sufficient. We wonder whether the authors have tested this method for themselves. The manipulative instructions, which are given very fully, seem generally sound, forming a particularly interesting part of the work, and the inclusion of methods, such as the use of the "cupferron" reagent in the estimation of iron, which are not usually met with in a text-book of this size, will show that the work is not lacking in originality.

Chemical equations are given whenever possible, and it is left to the student in most cases to calculate his results from these, a method preferable to the haphazard use of "factors," the significance of which the student may or may not appreciate.

With the exception of the omission of any reference to cobalt, this book is comprehensive, written in a very readable manner, and should have a distinct educational value.

Laboratoriumsbuch für die Industrie der Oele und Fette. By Dr. J. MARCUSSON. (Halle-a.-S., Wilhelm Knapp. Pp. 146. Price 6.60 Marks.)

Owing to the importance of the oil industry and the enormous advances in the employment of oils of all kinds which has taken place within the last few years, a book dealing with the analytical methods employed in the industry is sure of a ready reception—provided, of course, that it is a correct guide.

The book before us commences with a general description of the properties of oils, fats, and waxes. It must be made clear at this stage that the book does not deal with mineral oils except in so far as they are used as adulterants, but with vegetable and animal products. The first part of the book deals with the classification and chemical structure of oils and fats and their general properties, such as the properties of the saturated and unsaturated fatty acids which are found in fats.

The author then describes in detail the different tests employed in the analysis of oils and fats, in the first place, the physical methods such as specific gravity, melting-point, solubility, refraction, and so on.

Then he deals with the chemical tests, including the methods dealing with the determination of water, tests for mixture and mineral oils, and a very important section on the methods for distinguishing one oil or fat from another. As these processes require great care the author has been at pains to describe them with particular accuracy. This part of the book will in fact be found of very great value to the chemist who has to analyse oils, fats, and waxes. While the descriptions of the methods are accurate and sufficient they are not verbose, consequently the book is particularly useful for the laboratory, for which, of course, it is intended.

The third and final part of the book describes many of the methods employed in the works where the various oil and wax products are being manufactured. For example, there is a brief description of paraffin wax and the test methods employed to ascertain if it is of sufficient purity for the various purposes for which it may be required, and a similar note on bees-wax, wool fat, soaps, etc.

The book is a most useful laboratory guide, and we have no hesitation in highly recommending it to those engaged in the oil, fat, and wax industries, or those who have to analyse these products.

The Manufacture of Sulphuric Acid and Alkali. By GEORGE LUNGE, Ph.D., Vol. I, in three parts. Fourth Edition. (London, 1913 : Gurney & Jackson. Pp. 1,616. Price £3 3s. net.)

A new edition of this monumental work is again before us. The present book, being Vol. I, is divided into three parts, consisting together of 1,616 pages. Since the last volume was published in 1903 great strides have been made in nearly all the industrial processes included in the scope of the book. Dr. Lunge, with his incomparable knowledge of the subject, has incorporated these advances. The new subject matter is introduced into the text in the same lucid and interesting manner as has always been the charm of Dr. Lunge's books.

Part I commences with an introductory chapter on Historical and General Notes on the Manufacture of Sulphuric Acid. Chapter II deals with the raw materials. Under Sulphur there is an interesting section on the Frash process for extracting sulphur, which is found in such large quantities and at great depths in Louisiana. The introduction of this process has made the United States the leading sulphur-producing nation of the world. In England the bulk of the sulphur is obtained from Sicily, but as the cost of mining at Louisiana by the Frash process is cheaper than it can be produced in Sicily, quite likely in the near future we may be importing sulphur from the United States.

After dealing with sulphur and the different methods of obtaining it, Chili saltpetre and the manufacture of nitric acid follows. This section also deals with the production of nitric acid and nitrates by oxidation of atmospheric nitrogen. Reference is made to Ostwald's process for oxidizing ammonia by passing it over smooth platinum coated with platinum black.

Sulphuric acid is then treated in detail, and the whole of Part II is also devoted to its manufacture and purification. This is continued in Part III in so far as the chamber process is concerned, and then there is a very full account of the contact process.

In reviewing this monumental work the difficulties of the reviewer are

minimized, because every one knows the work of Lunge, and all the reviewer has to say is that the reputation of Lunge is maintained, and that he has in this last edition even surpassed himself ; greater praise could not be given. The work is a record of progress and industry magnificently written, which brings a vast subject up to date and places on record the enormous advances which have been made by the chemist and engineer in one of the most important branches of industry.

Photo-Electricity. The Liberation of Electrons by Light, with Chapters on Fluorescence and Phosphorescence, and Photo-chemical Actions and Photography. By H. STANLEY ALLEN, M.A., D.Sc. (London, 1913 : Longmans, Green & Co. Pp. 221. Price 7s. 6d. net.)

This book is one of a series of Monographs on Physics being issued under the general editorship of Sir J. J. Thomson and Dr. Frank Horton, and a very excellent example it is of the usefulness of such monographs in these days of extreme specialization, for without them it would be well-nigh impossible for the average man to get any exact knowledge at all outside the particular corner of the branch of science in which he himself works.

Although it may occupy a very small corner of physics, the phenomena of photo-electricity, all clustering round the simple fact that a negatively-charged body loses its charge when short wave-length radiation falls upon it, throw considerable light both on the nature of radiation and the structure of the atom, and some knowledge of the subject is therefore essential to a proper understanding of the fundamental problems of physics and chemistry. This is the aspect of the subject which will probably attract most attention from Dr. Allen's readers, and he deals with it in a very clear and interesting fashion in his chapters on "Theories of Photo-electric Action," "Fluorescence and Phosphorescence," and "Photo-chemical Actions."

It is interesting to note that Dr. Allen inclines to the view that the electrons concerned in the photo-electric effect are probably derived from those more or less closely bound up with the atom, and that the selective emission of these electrons is a resonance phenomenon—they are set in resonant vibration by the incident light, and acquire sufficient velocity to enable them to escape from the atom. He is not inclined to accept, for the time being, the only alternative which explains the proportionality between the number of electrons emitted and the intensity of the light, and the *independence* of the *velocity* of emission on that intensity; namely, the quantum or unitary theory of radiation associated with the names of Planck, Einstein, and Thomson.

Sufficient has been said to draw attention to the extreme interest of this book, and, with one reservation, to the admirable way in which the author, himself a distinguished investigator in this field, has presented his subject. The account given in every chapter of the experimental work that has been carried out on every aspect of photo-electricity is remarkably complete and comprehensive, but in many instances it is somewhat disconnected, because the various researches are merely abstracted in historical sequence instead of being collated into one continuous whole, and the references all banished to bibliographies at the end of every chapter. Certainly the conclusions to be deduced from the experimental results are afterwards summarized—for the benefit of the impatient reader ; and the criticism we feel bound to make is but slight compared with the thanks that are due to Dr. Allen for having given us so thorough and stimulating a study of his subject.

Rays of Positive Electricity and their Application to Chemical Analysis. [Monographs on Physics. Edited by Sir J. J. THOMSON and Dr. FRANK HUTTON.] By Sir J. J. THOMSON, O.M., F.R.S. (London, 1913: Longmans, Green & Co. Pp. 132. Price 5s. net.)

In this volume Sir J. J. Thomson has brought together an account of the brilliant series of researches that he has been carrying out for the past few years at the Cavendish Laboratory on the nature of the "Kanalstrahlen," which were discovered by Goldstein in 1886 as discharges behind a perforated cathode, and which have since been shown to consist of streams of positively-electrified particles of atomic and super-atomic dimensions. Needless to say the subject is of the greatest possible theoretical importance, a study of the positive rays throwing much light on the constitution of gases, the nature of molecules and inter-atomic forces, and the phenomena of ionization. But in the skilful hands of Sir J. J. Thompson these positive discharges have also become a valuable engine of chemical research, for by subjecting them at low pressures to powerful magnetic and electric fields applied simultaneously he has been able photographically to map out the paths of the separate molecules and so to determine their masses. Thus the presence of an exceedingly minute quantity of gas may be detected from a photograph of the positive rays in a discharge tube. The method has already produced results of great interest, firstly in the discovery of what appears to be a new element with an atomic weight 22—rather disturbing to the harmony of the Mendeleef scheme—and secondly in the detection of what is probably an allotropic, tri-atomic, form of hydrogen, H_3.

No chemist will wish to be unacquainted with this remarkable and stimulating work, and here he will find it all placed before him in convenient and agreeable form.

Oxidations and Reductions in the Animal Body. By H. D. DAKIN, D.Sc. (London, 1913: Longmans, Green & Co. Pp. 135. Price 4s. net.)

This new volume of the monographs on Biochemistry, edited by Plimmer and Hopkins, deserves a hearty welcome. The author is well known for his highly important contributions to our knowledge of oxidations and reductions in the animal body, and he has produced a book which will prove indispensable to all workers on the subject.

After a short introduction, the nature of the oxidizing and reducing agents of the body and the methods used in investigating the reactions of these substances are discussed. It is pointed out that recent work lends strong support to the theory that the active oxidizing agents in the body are of the type of superoxides. One striking piece of evidence in favour of this view is that the normal saturated fatty acids in the body undergo oxidation in the β position—butyric acid yielding aceto-acetic acid—and that hydrogen peroxide alone of all the various oxidizing agents brings about the same reaction. In later chapters the changes which the different types of acids (including fatty acids, amino- and hydroxy-acids), carbohydrates, purine derivatives, etc., undergo in the animal organism are fully discussed.

The book is clearly written and can be warmly commended, not merely to those interested in biochemistry, but to chemists in general. It contains numerous suggestions as to promising lines of investigation from the purely chemical standpoint.

The Sugars and their Simple Derivatives. By JOHN E. MACKENZIE, D.Sc., Ph.D. (London, 1913: Gurney & Jackson. Edinburgh: Oliver & Boyd. Pp. xvi + 242. Price 7s. 6d. net.)

The contents of this book are well described by its title. The first seven-

teen chapters contain a clear account of all the more important sugars and their simple derivatives. Chapter XVIII is devoted to Glucosides, Chapter XVI to Fermentation, and Chapter XX to Metabolism. The book is clearly written, well printed, and well got up. It is not evident, however, that the author's presentation of the subject offers any substantial advantage over those of his immediate predecessors, and in some respects it is less satisfactory than the best-known short account of the sugars recently reviewed in these columns. In particular, although the facts are well stated, there are few indications as to the blanks in our knowledge and of promising lines of research. This defect is perhaps due to the fact that the author, to judge from the index, has not himself made any substantial contribution to the subject of which he treats.

The important subject of the hydrolysis of the sugars deserves rather fuller treatment than is accorded to it in the book. It should be pointed out that the third "rule" of Wilhelmy that the "activity" of an acid is proportional to its concentration is by no means accurate. Moreover, the numbers given on p. 39 for the relative strengths of acids are only valid for one definite dilution.

Laboratoriumsbuch für die Anorganische Grossindustrie. By Dr. G. von Horst. (Halle-a.-S., Wilhelm Knapp. Pp. 119. Price 5.60 Marks.)

This useful laboratory guide deals with special analytical methods which are of particular use in technical analytical laboratories. A list of the subjects included will make this clear: analysis and sampling of coal and other heating materials, examination and purification of water for steam-raising purposes, sulphuric acid manufactory. Under this last heading the analysis of the raw materials, such as pyrites, sulphur, etc., is dealt with and then the analysis of the finished product and the analysis of the gases, acid, etc., during the course of the manufacturing operations. Then follows the manufacture of nitric acid and the various analytical operations required for the examination of the raw materials, such as Chili saltpetre, and so on Then the analysis of the finished product and the control analyses during the operation of manufacture. Hydrochloric acid and salt cake manufacture is then dealt with on similar lines to the above, that is to say, the analysis of raw materials, of the finished product, and so forth.

The Deacon Process for the manufacture of chlorine and the manufacture of bleaching powder follows.

Section VII is on the manufacture of ammonia and caustic alkali, artificial manures, analysis of fire and acid resisting materials. Finally there are a series of tables giving the specific weights of acids, the percentage of sulphur in pyrites and blende and so on.

The book will be found very useful in the technical laboratory, and we heartily recommend it. We might add that we have used it in the laboratory and found the methods sound and accurate.

Electric Furnaces in the Iron and Steel Industry. By Dipl. Ing. W. Rodenhauser, E.E., and I. Schoenawa. Authorized Translation and Additions from Advanced Sheets of the Second German Edition by C. H. Vom Baur, E.E. (New York, 1913: John Wiley & Sons. London: Chapman & Hall, Ltd. Pp. xv + 419. Price 15s. net.)

Although this book must to some extent be considered an *ex parte* statement on the present position of the electrometallurgy of iron and steel,

it can none the less be said that it will be found to be indispensable to the metallurgist who wishes to have in a compact form a fair and full account of present practice in this, perhaps the most promising direction of his art. The book is pre-eminently a practical one; that is to say, it describes and discusses processes in actual use, and when allowance is made for a very natural, but by no means unjustly expressed, bias in favour of the induction furnace in its modern form, the reader will find here all the data necessary to enable him to judge for himself as to the best type of furnace at present available for any particular end which he may have in view.

In its English form the book is intended to make a special appeal to the North American iron and steel manufacturer, in whose continent, we are told, the future of electric steel rails seems assured in view of their proved superiority over open-hearth and Bessemer rails. There seems to be no valid reason why the same causes should not operate in this country in extending the use of electrical methods of steel-making, and we can only hope that a careful study of this book will convince our more cautious countrymen that the electric steel furnace, now so widely in use both in America and on the Continent, where conditions after all are generally not so different to what they are here, has long passed the experimental stage and has really at length come to stay.

Most instructive are the tables on pp. 261 to 277, giving a complete list of the electric furnaces of all types now in use, showing their capacities, power consumption, and nature of charge and product. The figures given are of sufficient interest to summarize in the accompanying table.

Furnace.	Number in Use.	Approximate Power Consumption in Kilowatts.		
		Great Britain.	Continent.	America.
Héroult	31	800	12,000	6,500
Girod	19	—	6,400	—
Stassano	17	1,000	3,200	—
Keller	6	—	2,100	—
Other arc furnaces ...	15	350	3,900	600
Kjellin	15	580	2,400	330
Röchling-Rodenhauser...	20	—	6,500 (550 in Japan)	600
Other induction furnaces	4	—	1,300	—
Other furnaces	2	—	1,000	—
Totals	129	2,730	38,800	8,030

The book is excellently planned. After some short introductory chapters dealing with the laws of electricity so far as they are concerned in electric furnace practice, the general conditions for the operation of an "ideal" electric furnace are laid down. The arc furnace, first in general, and then the great types in present use, the Stassano, Héroult, and Girod, is then described in detail and its construction and operation at every stage compared with that of the "ideal" furnace already referred to. The induction furnace is then dealt with in the same fashion, the Kjellin and Röchling-Rodenhauser types (the latter usually a combined induction and resistance furnace) being

described in full detail and compared both with the "ideal" furnace and with the competing arc types. Chapters on the electric shaft furnaces of Keller, Stassano, and Héroult, and the more important Grönwell, Lindblad, and Stalhane furnace, which are intended to replace the ordinary blast furnace; on a few types of furnaces which are to a small degree in use; and finally the Tables of Statistics abstracted above, complete Part I of the book. Part II deals entirely with the practical details of furnace construction and operation.

We cannot here deal with the many debatable points raised in the course of the authors' discussion of the various types of furnace, but we imagine that, making every allowance for what the future will bring forth, many will dispute the statement (p. 76) that "the race in the open market has not proved the superiority of one or another furnace system," in view of the fact that some 88 arc furnaces with a power consumption of some 37,000 kw. are in present operation as against 41 induction furnaces consuming some 12,500 kw. The induction furnace, in its combined form, certainly has a future for special quality steels, but he would be a bold prophet who would assert, on present knowledge and experience, that it will be able to compete with the arc furnace, with its far greater possibilities in growth of capacity, for the manufacture of steel rails, if ever these, as they possibly will, come one day to be exclusively made in the electric furnace. But this opinion detracts in no way from the great value of what Messrs. Rodenhauser and Schoenawa have given us here out of the fulness of their experience, and for that every metallurgist will be grateful to them.

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition in Five Volumes. Vol. V, Sodium to Z. (London, 1913: Longmans, Green & Co. Pp. 830. Price £2 5s. per volume.)

All concerned deserve our heartiest congratulations on the completion of this great and useful work. Our judgment as to how extremely useful it is bound to be to every practical chemist—and the writer speaks as one who has occasion constantly to refer to it—has already been expressed on the appearance of the previous volumes and need not again be repeated.

A few of the articles of outstanding importance in the present volume are those on Sodium [Alkali Manufacture], Spectrum Analysis (with a full Bibliography—we are glad to note many more of these useful adjuncts than there were in the earlier volumes), Starch, Sugar, Sulphuric Acid, Synthetic Drugs, Triphenylmethane Colouring Matters, Vegeto-Alkaloids, Water: the names but indicate the range and value of this invaluable Dictionary.

Notes on Chemical Research. By W. P. Dreaper, F.I.C., F.P.S. (London, 1913: J. & A. Churchill. Pp. vii + 68. Price 2s. 6d.)

This little book consists of a series of articles which appeared originally in the "Chemical World." The seven chapters deal with such subjects as the selection of subject matter and methods of investigation, the application of chemical research to industry, and research in relation to analysis. The book contains many useful suggestions and a great deal of information, and can be cordially recommended to the young chemist.

Incandescent Lamps and their Application. By D. H. Ogley. (London, 1914: Longmans, Green & Co. Pp. 107. Price 2s. 6d. net.)

The subject-matter of this little book divides itself, roughly, into three parts: the first is devoted to definitions of the quantities involved and the elementary

principles of photometry, the second deals with the polar curve of intensity and the salient properties of carbon and metal filament lamps, and the third treats of the principles of vision and the fundamental canons of good lighting. The book is intended to appeal to the general reader who has no great stock of scientific knowledge, and much of the matter is well chosen to bring home to such a reader the differences between good and bad lighting. The illustrations, too, are well selected in this respect and the fact that many of them have already appeared elsewhere is no demerit.

The writer seems, however, to have been singularly unfortunate in the revision of his work : his style is frequently very cumbersome and there are many slips in his English—minor blemishes which in a text-book may easily be condoned. But the work is also marred by some inaccuracies in points of fact, and we fear that these will cause much trouble and perplexity to the reader who takes up this book with no previous knowledge of the subject.

Physical Chemistry and Scientific Thought. By Professor W. C. McC. Lewis, M.A., D.Sc. (The University Press of Liverpool, 57, Ashton Street. Pp. 20. Price 1s.)

This is a reprint of the Inaugural Lecture delivered by the new Brunner Professor of Physical Chemistry at the University of Liverpool on January 16th last. In the opinion of Professor Lewis the chemical and physical advances of the future will be made by the simultaneous application of concrete mechanical notions and the more abstract conclusions of energetics. Such a union of kinetics and thermodynamics has already led, in the hands of Planck, Einstein, Nernst, and others, to the recent remarkable advances in our knowledge of the solid state. As regards the study of systems not in equilibrium, Dr. Lewis thinks no fields will repay investigation more surely than those of photo-chemistry and chemical affinity.

The research student should read and carefully ponder over the words of this thoughtful and suggestive Address.

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